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An Investigation of the Effect of the Addition of Salts on the Ph Values of Dilute Acids

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THE EFFECT OF THE ADDITION OF SALTS ON THE pH VALUES OF DILUTE ACIDS

PREFACE

This work on the effect of the addition of salts on the pH values of dilute acids was done at the College of William and Mary during 1932 and 1933.

The purpose of the investigation was to find the effects of the addition of different salts on the pH values of dilute acid solutions.

The effects were measured by the use of the hydrogen electrode and saturated calomel cell, and further checked by the use of the quinhydrone electrode with the calomel cell. The voltages were determined by the use of the potentiometer and the pH values were then computed and compared.

The writer is greatly indebted to Dr. W. C. Cuy, Professor of Chemistry, of William and Mary College, for his guidance and assistance throughout the investigation.

INTRODUCTION

The problem chosen for investigation was the effect of the addition of various salts on the pH values of dilute acids. The acids used were hydrochloric (approximately 0.1 normal) and sulphuric (approximately 0.1 normal).

The degree of acidity is expressed in pH. Solutions with a pH of 7 are neutral; those having a pH of less than 7 are acid, and those having a pH of more than 7 are basic.

According to the mass law, the addition of a salt which contains a common ion should decrease the hydrogen-ion activity of the solution. Experiments, however, have shown that this does not always hold true.

Harned[1], for example, has studied cells of the type used in this investigation; that is

$$Pt\ .\ H_2 \left| \begin{matrix} HCl \\ N\ Cl \end{matrix} \right| \text{Saturated KCl} \left| \begin{matrix} N\ KCl \\ Hg_2Cl_2 \end{matrix} \right| Hg$$

in which the effect of the addition of certain salts, such as lithium chloride, potassium chloride, strontium chloride and calcium chloride was measured. Harned found that the addition

(1) A discussion of Harned's investigation may be found in Experimental Physical Chemistry by Daniels, Mathews & Williams, page 192, with reference to the Journal of American Chemical Society, 37:2460 (1915); 38:1986 (1916); 42:1808 (1920).

of the neutral salt resulted in a decrease of the electromotive force of the cell and he decided that the ionic activity of the hydrogen-ion was increased.

V. A. Arkadiev made an electrometric investigation of the influence of neutral salts on the potential of the hydrogen electrode. Chemical Abstracts, Vol. 17, June-Oct., 1923, page 2832, summarizes his work thus:

> "The influence of neutral salts on the potential of the hydrogen electrode is to increase its value. The increase being proportional to the concentration of the salt. For equivalent concentrations of neutral salts, the influence on the potential runs parallel to the tendency of the salts to form hydrates. The influence of KBr and LiBr is more marked than that of KCl and LiCl."

A. Sabrodina, Jaroslaw Przeborowski, and M. Fleissner also made investigations on the influence of neutral salts on the hydrogen electrode. Chemical Abstracts, Vol, 18, Jan.-May, 1924, page 955, gives the following on their work:

> "The effects of 0.1 N and 0.01 N solutions of HBr containing KNO_3, KCl, KBr, $NaNO_3$, NaCl, LiCl, and LiBr upon the potential of the hydrogen electrode are:
>
> increases with increase in the concentration of the salt;
>
> increases with solubility, hygroscopicity and ease of hydrate formation of the series; is greater with bromide than with chloride.
>
> It is concluded that only unhydrated H ions have an effect on the hydrogen electrode, and that the influence of the salts either as ions or as mols lies in their relative abilities to dehydrate the H ions."

L. Michaelis and M. Mizutani did work on the same subject, and in Chemical Abstracts, Vol. 19, for June-Oct. 1925, page declare that:

> "With very dilute HCl. In general with decreasing salt concentration the potential difference rises to a maximum in the region 0.2 - 0.3 N and then falls, so much so in some cases that the solution would appear to be more "acid" in the presence of salt than alone.
>
> From the results obtained with the alkali chlorides the effect of the different alkali ions is correlated symbolically with the atomic weight."

In this investigation data is also given on the effect of various mixtures of chlorides on dilute hydrochloric acid. The original manuscript is printed in "Z physick Chem." 113: 69-92, 1924.

A considerable amount of work has been done on measurements with the hydrogen electrode. Some of the outstanding work is that of Clarke E. Davis and Glenn M. Davidson on Studies of Hydrogen Ion Concentration Measurements, which is found in the Journal of the American Chemical Society, July-Dec., 1920, page 2065.

H. T. Beans and L. P. Hammett have done work which is described in the Journal of the American Chemical Society, Vol. 47, Jan.-June, 1925, page 1215. The subject of their investigation is Experimental Studies on the Hydrogen Electrode. It is an investigation which attempts to classify some of the conditions which give rise to variable potentials of hydrogen electrodes with platinum catalysts and to show how the variability may be eliminated. They discuss the various sources of error in measuring the pH of solutions. Oxygen has a great effect on the pH of alkali solutions, but, since the solutions used in this study were acid, the effect of oxygen should not be so great.

The results of this investigation of the effect of the addition of various salts on the pH of approximately 0.1 normal acids seem to have agreed with the work of Harned and others who have experimented with the same problem. The method used in this experiment was as follows:

The hydrogen and saturated calomel electrodes were dipped into the acid, the pH of which was to be measured. These were connected as shown by a drawing (Figure 3), which is given later on in detailed description of the procedure. The hydrogen was kept passing through the acid at a constant rate. Readings were taken on the potentiometer only when a constant point had been reached, and when the galvanometer showed no deflection. The salt was added to the acid in carefully weighed amounts, readings being taken after each addition after constancy had been reached. In most cases salts were added until saturation was reached. The pH values were then worked out from the formula:

$$pH = \frac{V - v - 0.00076\ t}{0.0001983\ T}$$

where "V" was the observed potential in volts, "v" the potential of the saturated calomel cell at the temperature of the experiment, "t" the temperature on the Centigrade scale, and "T", the Absolute temperature.

The mols of the salt added were computed and plotted against the pH values, as derived from the above formula.

Besides using the hydrogen electrode, the writer also experimented with the quinhydrone electrode. The quinhydrone electrode was used as a check on the work done with the hydrogen electrode. Salts that could not be used with the hydrogen electrode on account of poisoning could be used in the quinhydrone method.

The pH values for the quinhydrone readings were computed from the formula:

$$pH = \frac{0.7177 - 0.00074t - Y - v}{0.0001983\ T}$$

where "t" equals the Centigrade temperature, "Y" the observed potential in volts, "v" the potential of the calomel cell, corrected for temperature, and "T" the Absolute temperature at the time the experiment was performed.

As before, these pH values were plotted against the mols of salt added. The conclusions were arrived at after comparing the results of the experiment.

EXPERIMENTAL PROCEDURE

The following apparatus was set up according to the diagram shown in Figure 4:

Potentiometer
Galvanometer
Standard Cell
2 dry cell batteries
Hydrogen electrode
Calomel electrode
Hydrogen generator
Resistance box (400 ohms)
1 two-way switch
2 key switches
Resistance coil (for protection of potentiometer)
Rubber tubing
Copper wire (insulated)
4 washing bottles for gas
Beakers to hold sample

A solution of hydrochloric acid (approximately 0.1 normal) had been prepared, as had one of sulphuric acid (approximately 0.1 normal). The hydrochloric acid was used for finding the effect of chlorides on it. The sulphuric acid was to be used with the sulphates in the same manner.

The effects of some of the chlorides on the sulphuric acid were also tried as an interesting comparison.

The hydrogen and calomel electrodes (Figures 1 and 2 respectively) were first connected with the apparatus for generating the hydrogen gas. Especial care was taken to purify the hydrogen by passing it through four consecutive gas washing bottles which contained a fifty per cent solution of potassium hydroxide, mercurous chloride (saturated), potassium hydroxide and pyrogallic acid, and distilled water, respectively.

Figures 3 and 4 show the set-up of the apparatus as used. It was checked against the Standard Cell in the following manner:

First, the working current was adjusted through the potentiometer. This was done by throwing switch "S" to the "Std. Cell" position and setting the dial and slide wire, "A" and "B", to the voltage of the Standard Cell. The experimenter kept in mind the fact that the voltage of the two dry cells was approximately 3 volts and that the internal resistance of the potentiometer was about 160 ohms, and set the 4-dial rheostat to give approximately 0.01 ampere through the potentiometer. This meant that there was approximately [illegible]0 ohms in the 4-dial resistance box. Then K_1 was tapped and final adjustments were made on the rheostat.

The potentiometer was then ready to begin taking measurements. This procedure was repeated before each set of measurements was made, and occasionally checked while a set was being taken.

The buffer solution was placed in a 50 cc. beaker in which were immersed the hydrogen and saturated calomel electrodes. Hydrogen gas was allowed to pass through for sufficient time for the potentiometer reading to become constant, and there was no deflection of the galvanometer. This point was reached by adjusting the resistance in the potentiometer, first while tapping K_1 and then making the final adjustments while tapping K_2. This potentiometer reading was obtained by placing "S" in position "E.M.F.", as shown in Figure 3, and tapping K_1 and noting the galvanometer deflection. The deflection was reduced, or made zero, by adjusting dial switch

"A" and slide wire "B". Then K_2 was tapped and slide wire "B" was again adjusted until the galvanometer showed no deflection. The sum of the reading of the dial switch and slide wire gave directly the voltage being measured.

To make sure that the current through the potentiometer had not changed, switch "S" was returned to the "Std. Cell" position and the dial switch and slide wire were set to the voltage of the standard cell and K_2 was closed. If there was a small deflection the rheostat was adjusted to reduce the deflection to zero.

The pH of the Buffer solution as found by the formula:

$$pH = \frac{X - y \text{ [illegible]} 0.00076t}{0.0001985\ T}$$

showed that the apparatus was in good order.

The buffer solution was replaced by 35 cc. of tenth normal hydrochloric acid, which was run in from a calibrated burrette. The potential of the hydrochloric acid was measured and recorded after a constant point was reached. Constancy was usually reached in about ten minutes. Then the effect of the addition of sodium chloride to the acid was tried, beginning with a very small amount of the salt, carefully weighed out, and continuing until the saturation point was reached. Table I and Graph 1 give the data for this part of the experiment. They show that the acidity decreased at first, due to the effect of the addition of the common ion. This was soon overcome, however, and the solution became decidedly more acid.

This procedure was repeated with other salts and the results may be summed up as follows:

(a) Sodium chloride added to hydrochloric acid shows a decrease in E.M.F. which is followed by a steady increase as more salt was added. (See Graph 1 and Table I).

(b) Ammonium chloride added to hydrochloric acid shows a slight decrease followed by an increase in E.M.F. (See Graph 2 and Table II).

(c) Lithium chloride added to hydrochloric acid shows apparently no decrease at first, but the E.M.F. increases more rapidly than with any of the other salts used. (See Graph 3 and Table III).

The action of sulphates on tenth normal sulphuric acid was tried with the same apparatus, with the following results:

(a) Potassium sulphate added to sulphuric acid decreased the acidity at first, but increased it after a certain point. (See Graph 4 and Table IV).

(b) Sodium sulphate (crystalline) added to sulphuric acid decreased the acidity rapidly at first, but more slowly after reaching a certain point. (See Graph 5 and Table V).

(c) Sodium chloride with sulphuric acid decreased the acidity until saturation was reached. (See Graph 6

and Table VI).

(d) Lithium chloride with sulphuric acid increased the acidity. (See Graph 7 and Table VII).

(e) Potassium chloride with sulphuric acid increased the acidity. (See Graph 8 and Table VIII).

The effect of the addition of certain sulphates to sulphuric acid is worthy of study. Sulphuric acid is a much weaker acid than hydrochloric acid, yet it cannot be considered a weak acid in the same sense as acetic acid. When a chloride is added to hydrochloric acid, an increase in hydrogen-ion activity results. With the addition of sulphates to sulphuric acid, interesting intermediate effects are procured.

"In some cases, for example", says Daniels, Mathews and Williams, in Experimental Physical Chemistry, page 198, "when copper sulphate or nickel sulphate are added to sulphuric acid, the hydrogen electrode will not function in the solution and it is necessary to resort to the quinhydrone electrode. The quinhydrone electrode also makes possible the study of the effect of various salts, which would interfere with the hydrogen electrode or the hydrogen-ion activity of hydrochloric acid, thereby increasing the number of salts which may be used as solutes."

The quinhydrone electrode was then used to measure the effects of some of the salts that could not be measured with the hydrogen electrode. The quinhydrone method was also used as a check on previous work by using the same acids and salts, the pH values of which had already been determined by the bubbling hydrogen elec-

trode method. The quinhydrone electrode used was of the gold-wire type. It replaced the hydrogen electrode in the experimental procedure.

The working current was checked by means of the standard cell in the same manner as formerly described. Quinhydrone crystals were stirred into each sample before the measurements were made. A very small amount of the quinhydrone was needed to saturate the samples. Care was taken that the temperature of the solution and of the calomel cell were the same.

With the quinhydrone electrode, the voltage became constant within two or three minutes, whereas with the hydrogen electrode it took ten minutes, or even more, to reach a fairly constant value. It was noticed that the addition of some of the salts affected the temperature of the samples used. In some cases it was necessary to heat the sample in order to bring it to room temperature, and in others, to cool it.

The results obtained with the quinhydrone electrode were as follows:

(a) Potassium chloride with sulphuric acid increased the acidity. (See Graph 9 and Table IX).

(b) Sodium chloride with sulphuric acid increased the acidity more rapidly than potassium chloride. (See Graph 10 and Table X).

(c) Potassium sulphate added to sulphuric acid decreased the acidity at first, but more slowly as saturation was reached. (See Graph 11 and Table XI).

(d) Crystalline copper sulphate added to sulphuric acid decreased the acidity at first, but increased it after a certain point was reached. (See Graph 12 and Table XII).

(e) Anhydrous copper sulphate decreased the acidity at first, and increased it after a certain point was reached. (See Graph 13 and Table XIII).

(f) Sodium sulphate (with ten molecules of water) added to sulphuric acid decreased the acidity. (See Graph 14 and Table XIV).

(g) Zinc sulphate with sulphuric acid decreased the acidity, followed by an increase. (See Graph 15 and Table XV).

(h) Magnesium sulphate with sulphuric acid decreased the acidity, followed by an increase. (See Graph 16 and Table XVI).

(i) Lithium chloride with sulphuric acid gave a steady increase in acidity. (See Graph 17 and Table XVII).

Three of the measurements taken with the hydrogen electrode were checked with the quinhydrone electrode. These results are given in Graphs 18, 19 and 20 and in Tables XVIII, XIX and XX.

Two calomel electrodes were used. The first electrode was used for all of the measurements taken with the hydrogen electrode, and for some of the quinhydrone measurements. When the second electrode was used, the results are marked "Calomel Electrode No. 2".

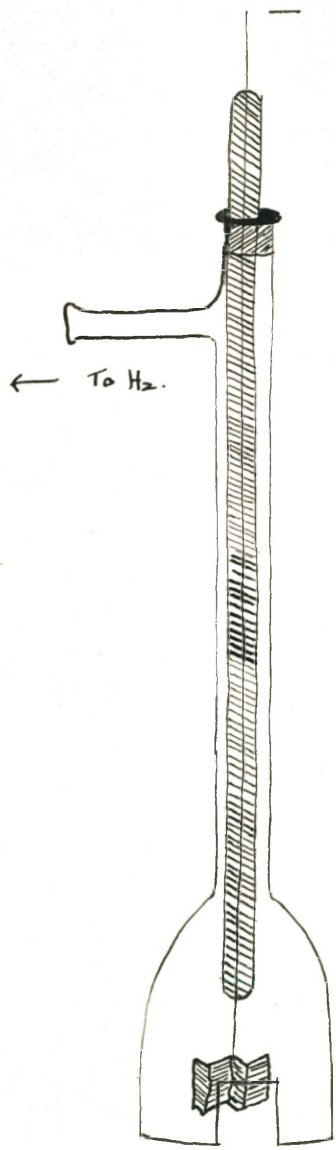


FIGURE I. THE HYDROGEN ELECTRODE.

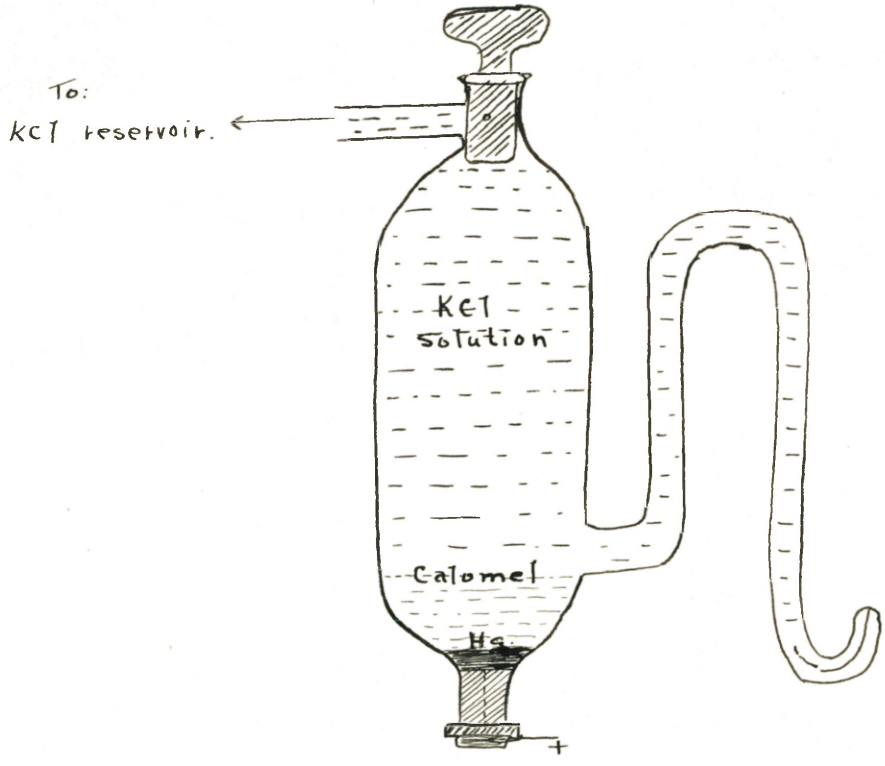


FIGURE 2. THE CALOMEL ELECTRODE.

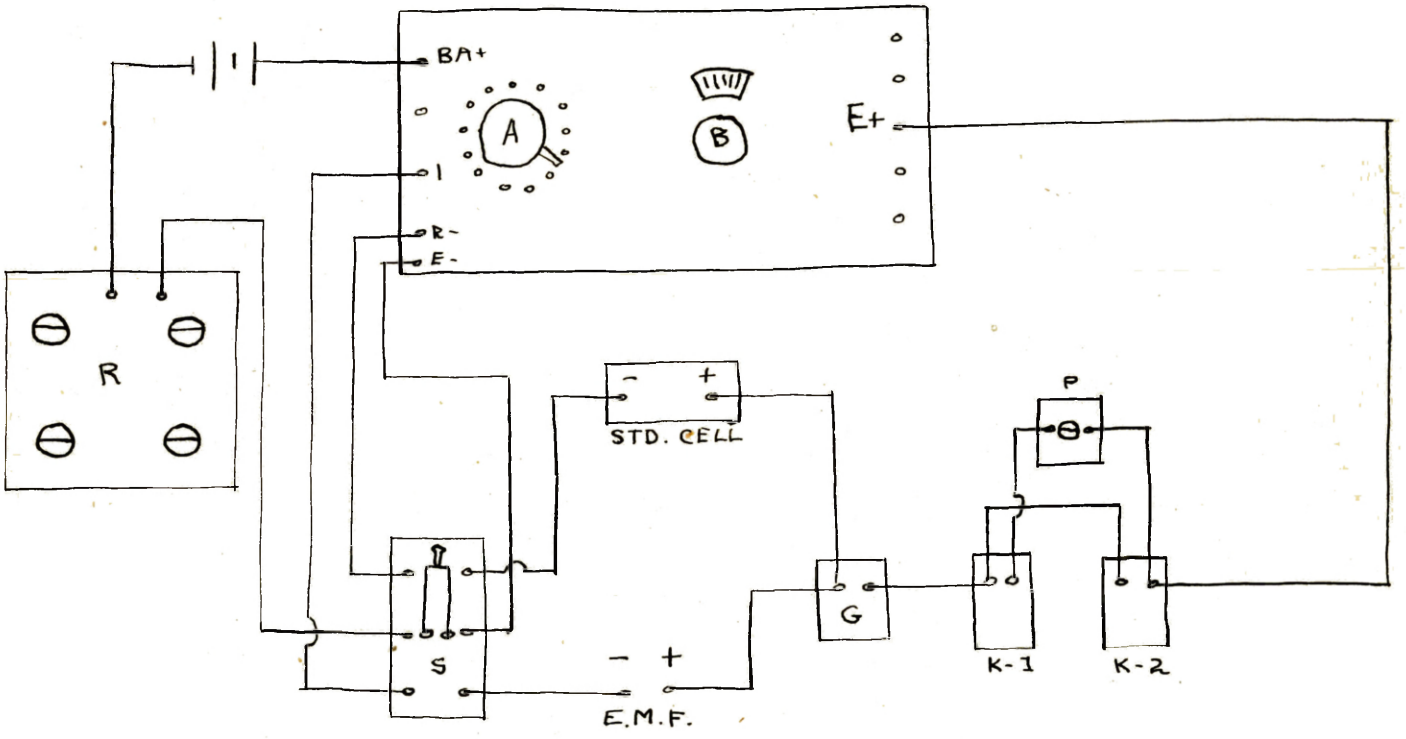


FIGURE 3. DIAGRAM OF WIRING USED IN THE DETERMINATION OF pH VALUES.

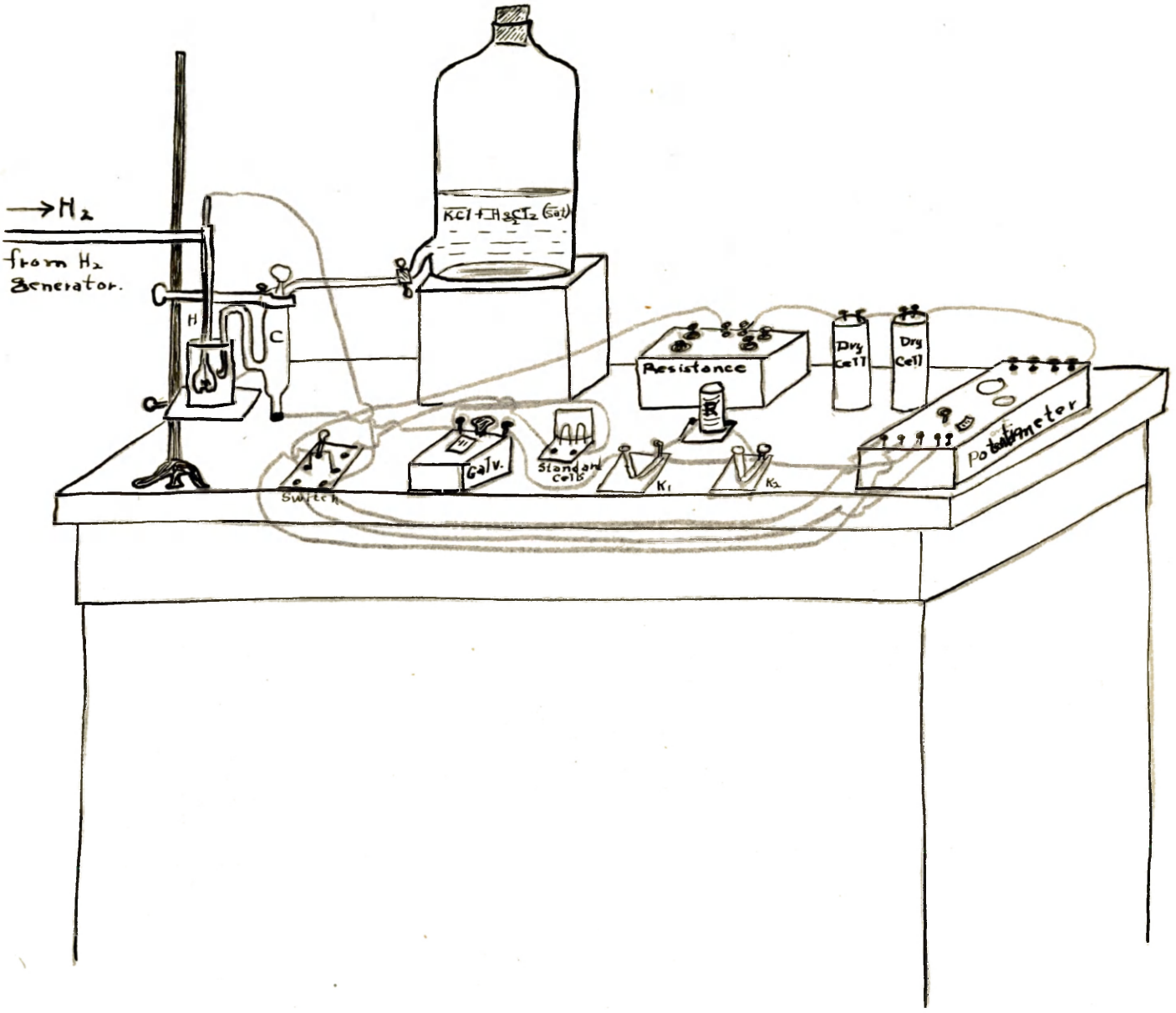


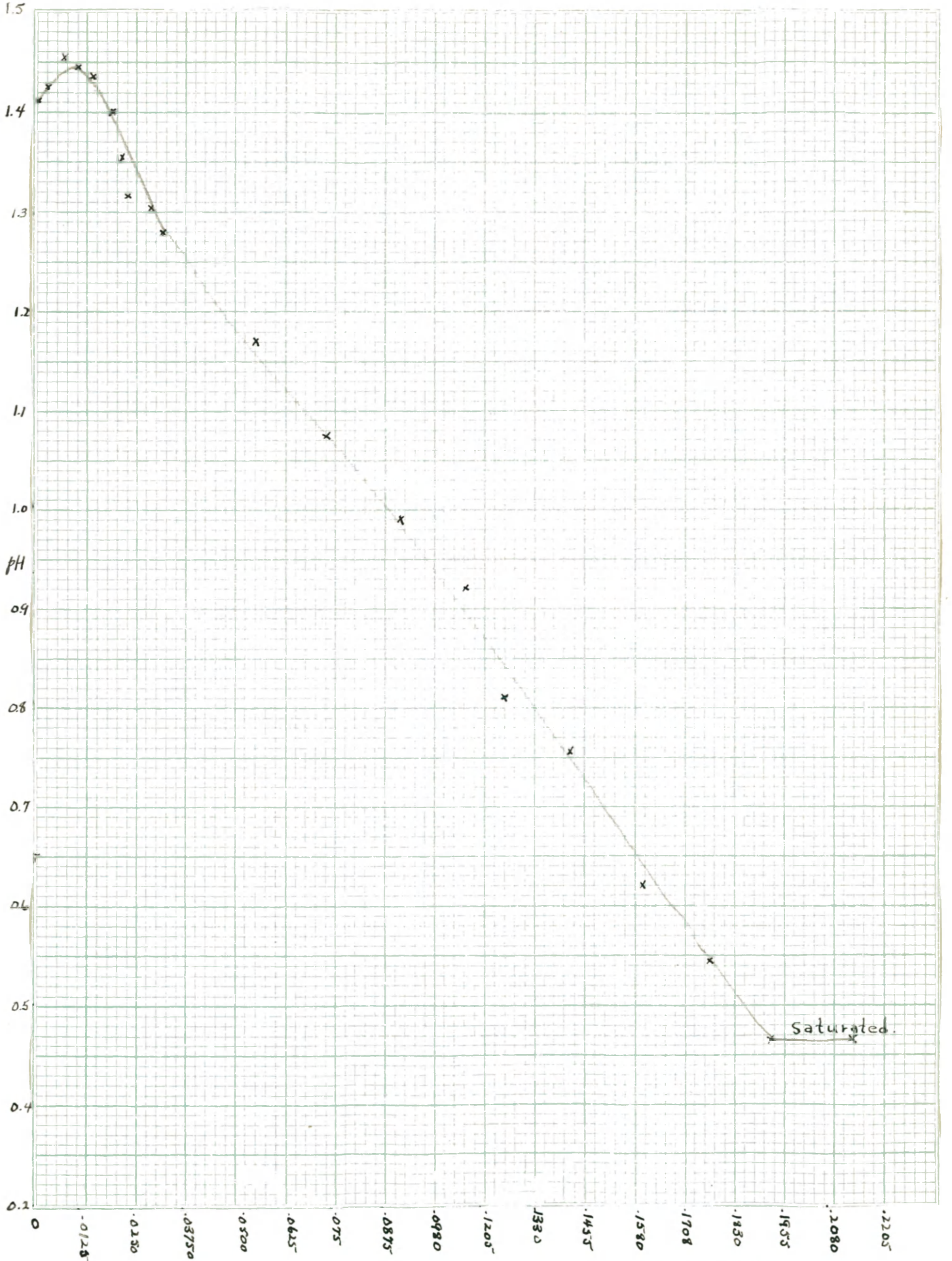
FIGURE 4 . APPARATUS USED IN THE DETERMINATION OF pH VALUES.

TABLE I

NaCl with 35 cc. 0.1 N HCl t is 28.5 degrees C.

(Hydrogen electrode)

NaCl (Grams)	Mols NaCl	Volts I	Volts II	pH
0.0	0.0	0.3005	0.3005	1.413
0.2	0.0034	0.3012	0.3012	1.428
0.4	0.0068	0.3037	0.3028	1.469
0.6	0.0102	0.3038	0.3025	1.472
0.8	0.0136	0.3021	0.3017	1.445
1.0	0.0170	0.3000	0.2997	1.408
1.2	0.0204	0.2970	0.2968	1.358
1.4	0.0238	0.2945		1.316
1.6	0.0272	0.2920		1.308
2.0	0.0340	0.2882	0.2924	1.278
2.4	0.0408	0.2814		1.264
3.4	0.0578	0.2697		1.169
4.4	0.0748	0.2603	0.2797	1.073
5.4	0.0918	0.2750		0.990
6.4	0.1088	0.2708		0.919
7.4	0.1258	0.2642	0.2650	0.809
8.4	0.1428	0.2610		0.756
9.4	0.1598	0.2585		0.613
10.4	0.1768	0.2488	0.2480	0.542
11.4	0.1938	0.2455	0.2455	0.485
12.4	0.2108	0.2436	0.2434	0.465



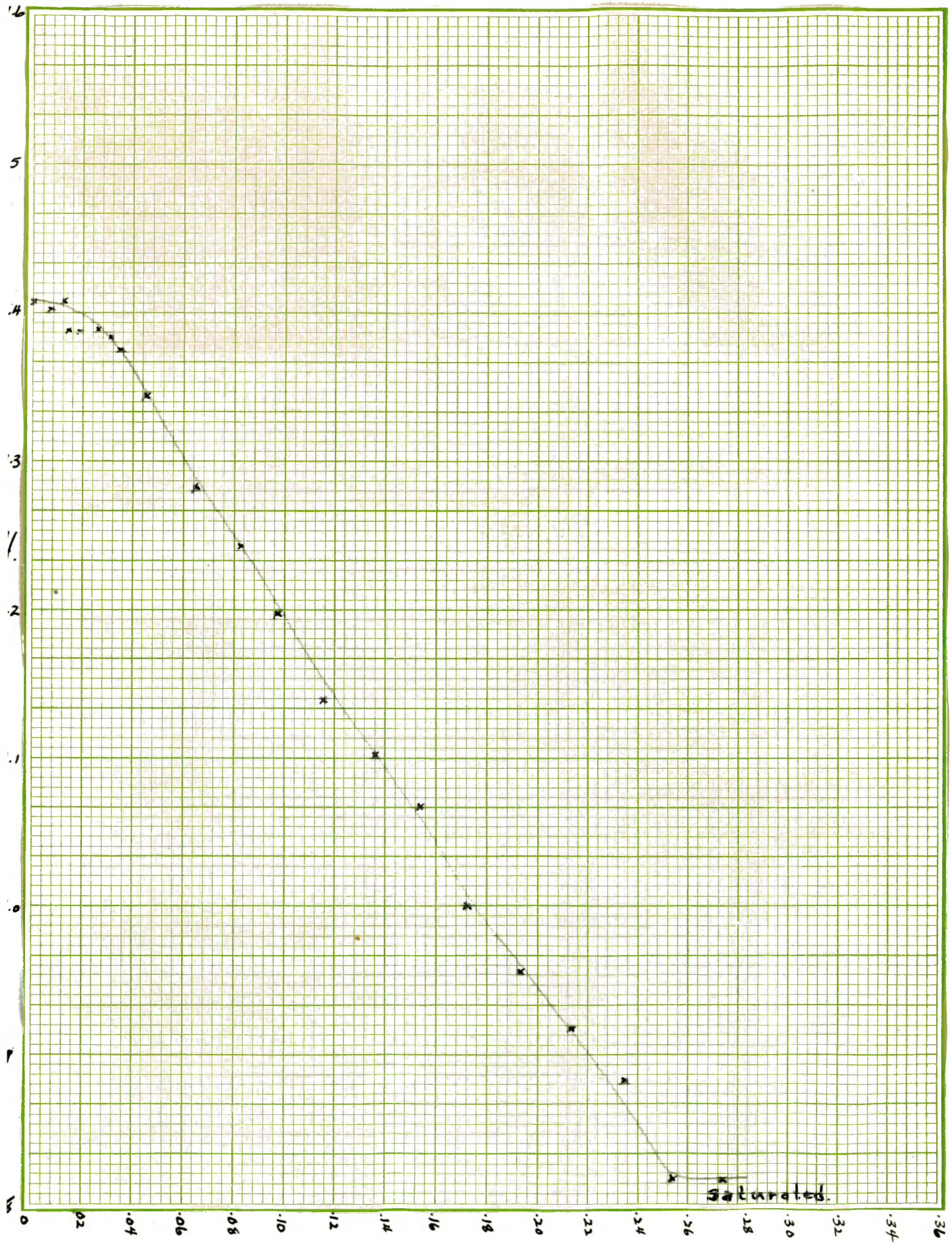
Graph 1. No. mols NaCl added to 35 cc. HCl.

TABLE II

NH_4Cl with 35 cc. 0.1 N. HCl (Hydrogen electrode)

t for Volts I 30° C.
t for Volts II 28.5° C.

NH_4Cl (Grams)	Mols NH_4Cl	Volts I	Volts II	pH
0.0	0.0	0.3008	0.3008	1.415
0.2	0.0037	0.3007	0.3007	1.408
0.4	0.0074	0.3005	0.3005	1.416
0.6	0.0111	0.2986	0.2988	1.388
0.8	0.0148	0.298	0.2985	1.385
1.2	0.0222	0.2978	0.2978	1.368
1.6	0.0296	0.2964	0.2964	1.361
2.0	0.0370	0.2971	0.2975	1.366
2.4	0.0444	0.2955	0.2955	1.338
3.4	0.0629		0.2935	1.304
4.4	0.0814	0.2901	0.2897	1.236
5.4	0.0999		0.2875	1.199
6.4	0.1184	0.2846	0.2840	1.14
7.4	0.1369		0.2820	1.107
8.4	0.1554	0.2788	0.2795	1.062
9.4	0.1739		0.2758	1.005
10.4	0.1924	0.2742	0.2731	0.958
11.4	0.2109		0.2711	0.925
12.4	0.2294	0.2671	0.2672	0.879
13.4	0.2479	0.2647	0.2644	0.813
14.4	0.2664	0.2647	0.2644	0.813



Graph 2. Mols NH_4Cl added to 35 cc. HCl

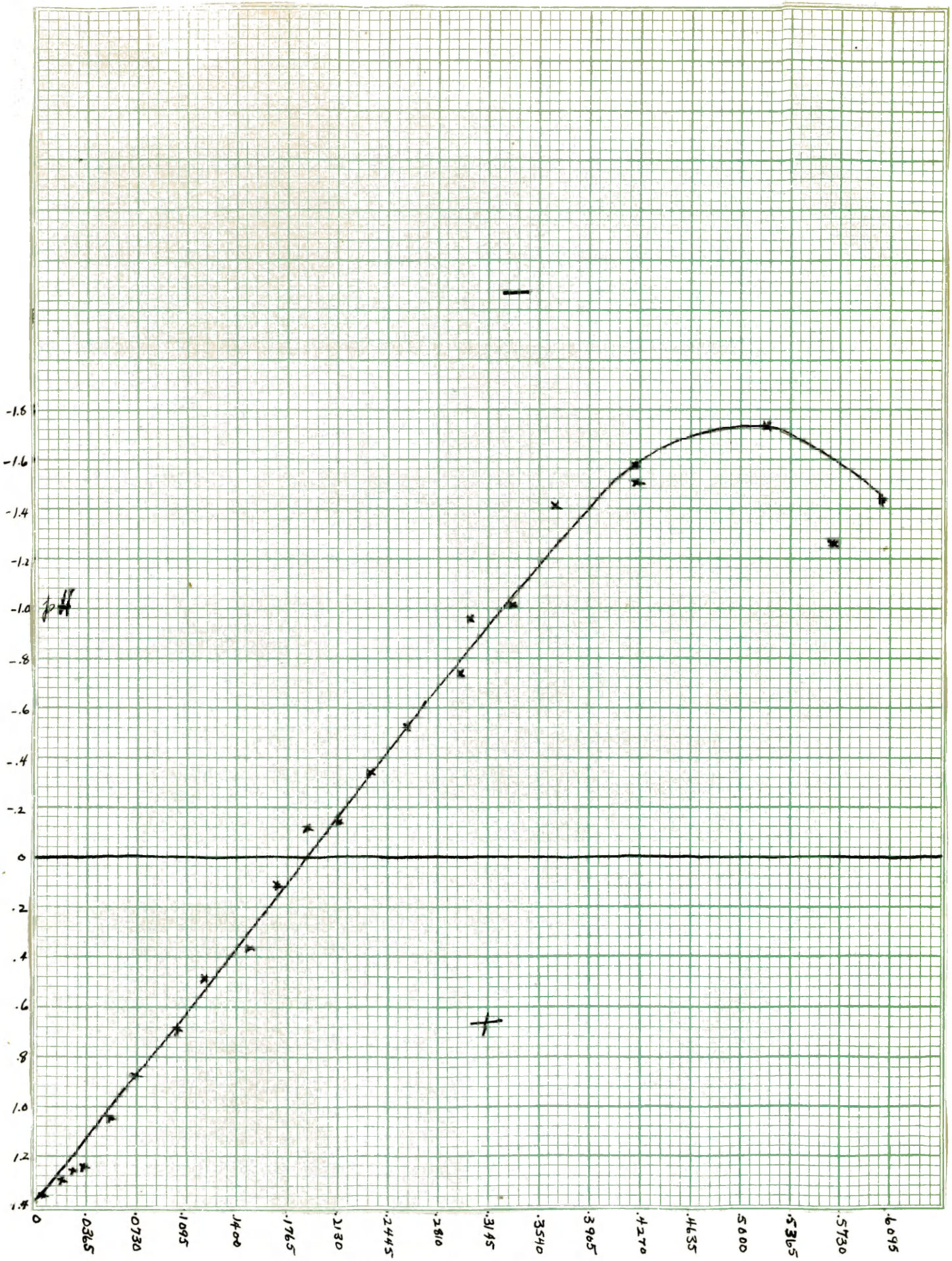
TABLE III

LiCl with 35 cc. 0.1 N. HCl (Hydrogen electrode)

t for Volts I is 29.5° C.

t for Volts II is 28° C.

LiCl (Grams)	Mols LiCl	Volts I	Volts II	[illegible]
0.0	0.0	0.296	0.2973	1.552
0.2	0.0047	0.2964	0.2970	1.547
0.4	0.0094	0.2945	0.2947	1.308
0.6	0.0141	0.2913	0.2918	1.259
1.0	0.0236	0.2881	0.2895	1.218
2.0	0.0472	0.2736	0.2797	1.057
3.0	0.0708	0.2677	0.2681	0.865
4.0	0.0944		0.2576	0.657
5.0	0.1180		0.2447	0.471
6.0	0.1416		0.2379	0.357
7.0	0.1652		0.2287	0.108
8.0	0.1888		0.2088	-0.141
9.0	0.2124		0.2072	-0.157
10.0	0.2360		0.1972	-0.387
11.0	0.2596		0.1845	-0.541
12.0	0.2832		0.1695	-0.791
13.0	0.3068		0.1595	-0.988
14.0	0.3304		0.1486	-1.191
16.0	0.3776		0.1318	-1.48
18.0	0.4248		0.1218	-1.668
20.0	0.4720		0.1251	-1.653
22.0	0.5192		0.1115	-1.760
24.0	0.5664		0.1440	-1.816
26.0	0.6136		0.1314	-1.427



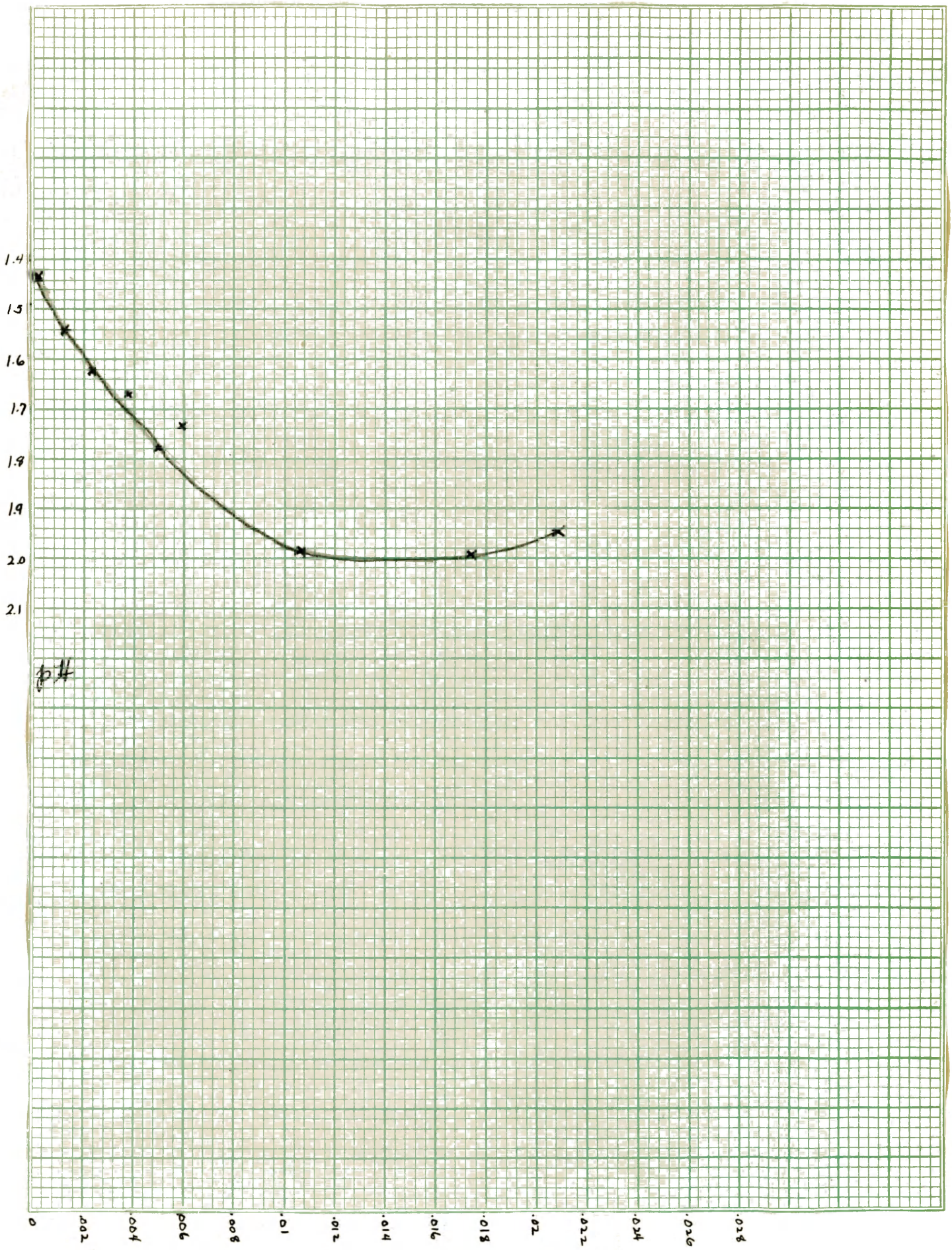
Graph 3. Mols LiCl added to 35 cc. 0.1 N HCl.

TABLE IV

K_2SO_4 with 35 cc. 0.1 N. H_2SO_4 t for Volts I 29° C.

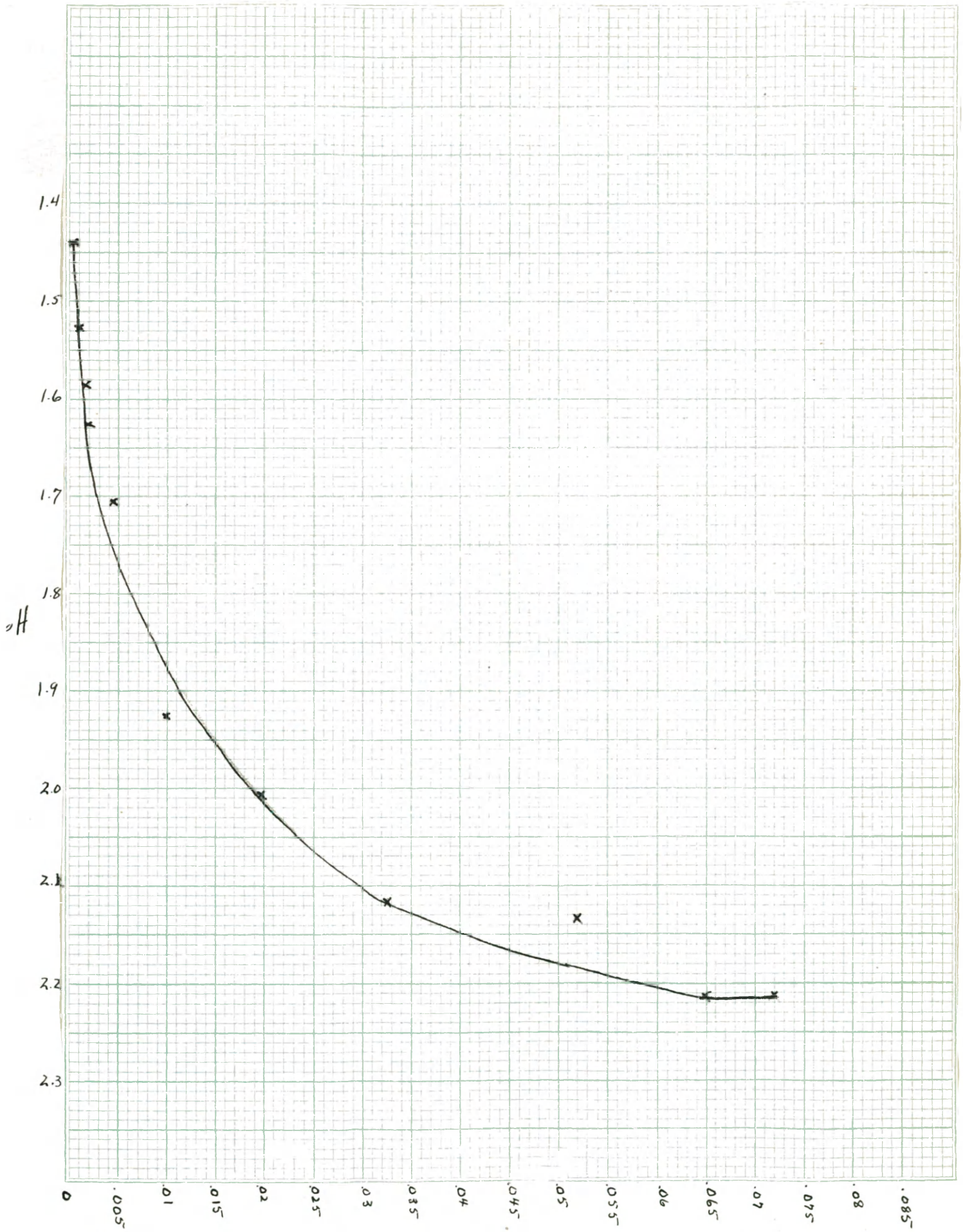
(Hydrogen electrode) t for Volts II 29° C.

K_2SO_4 (Grams)	Mols K_2SO_4	Volts I	Volts II	pH
0.0	0.0	0.3025	0.3030	1.457
0.2	0.00115	0.3089	0.3092	1.564
0.4	0.00230	0.3150	0.3155	1.499
0.6	0.00345	0.3175	0.3205	1.706
0.8	0.00460	0.3197	0.3257	1.744
1.0	0.00575	0.3240	0.3284	1.816
2.0	0.0115	0.3399	0.3401	2.082
3.0	0.0172	0.3485	0.3484	2.230
4.0	0.023	0.3538	0.3540	2.314
5.0	0.0287	0.3550		2.301
6.0	0.0345	0.3550		2.301



Graph 4. Mols K_2SO_4 added to 35 cc. 0.1 N HCl.

Graph 5.

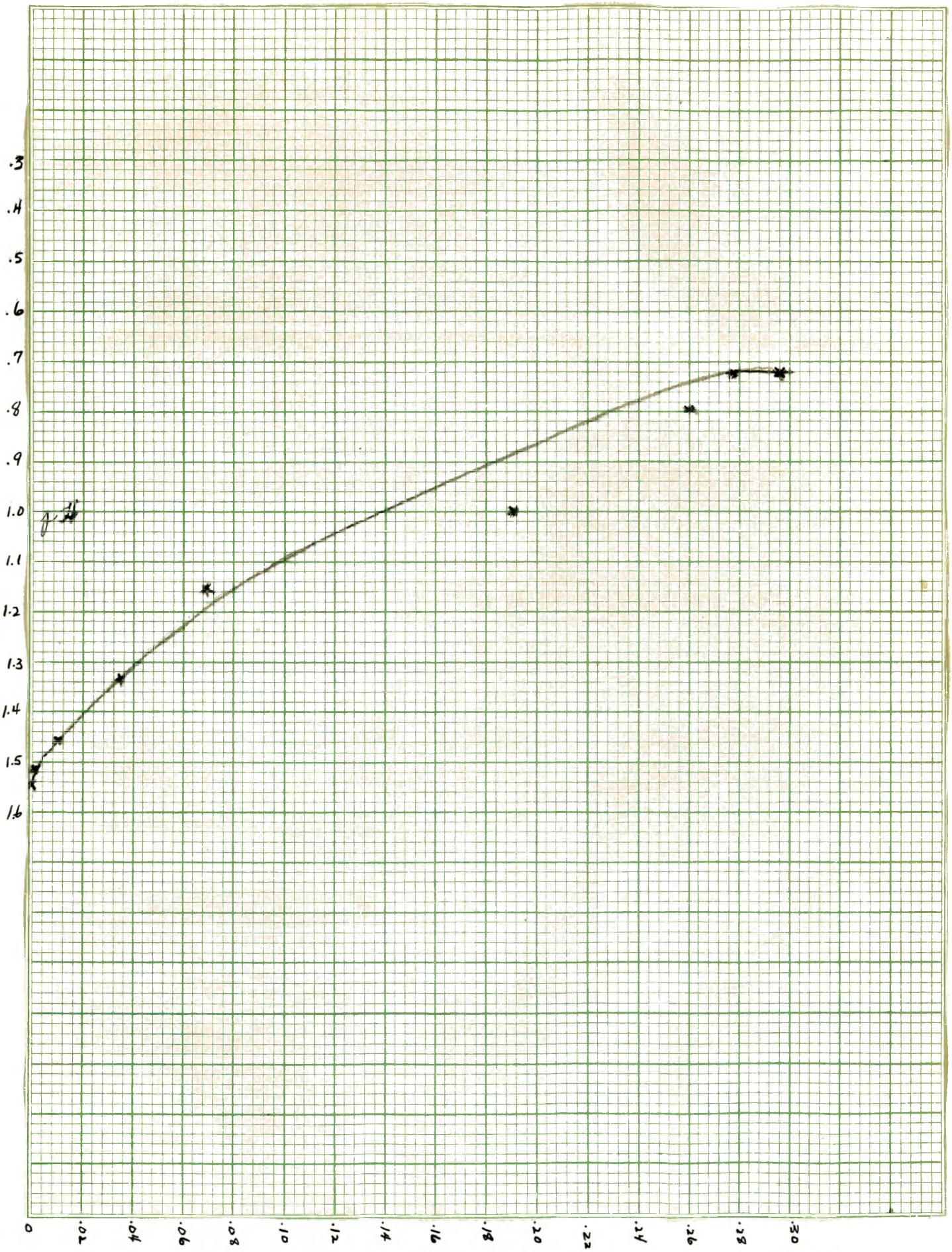


Graph 5. Mols $Na_2SO_4 \cdot 10\,H_2O$ added to 35 cc. 0.1 N H_2SO_4.

TABLE VI

NaCl with 35 cc. 0.1 N. H_2SO_4 t is 27.5° C.
(Hydrogen electrode)

NaCl (Grams)	Mols NaCl	Volts I	Volts II	pH
0.0	0.0	0.3088	0.3097	1.582
0.2	0.00342	0.3086	0.3086	1.529
0.4	0.00684	0.3068		
0.6	0.01026	0.3044	0.3051	1.471
1.0	0.0171	0.3006	0.3007	1.397
2.0	0.0342	0.2938	0.2974	1.342
3.0	0.0513	0.2898		
4.0	0.0684	0.2787	0.2865	1.159
6.0	0.1197	0.2682		
8.0	0.1881	0.2569	0.2774	1.007
11.0	0.2394		0.2645	0.799
12.0	0.2565		0.2606	0.725
13.0	0.2736		0.2605	0.725

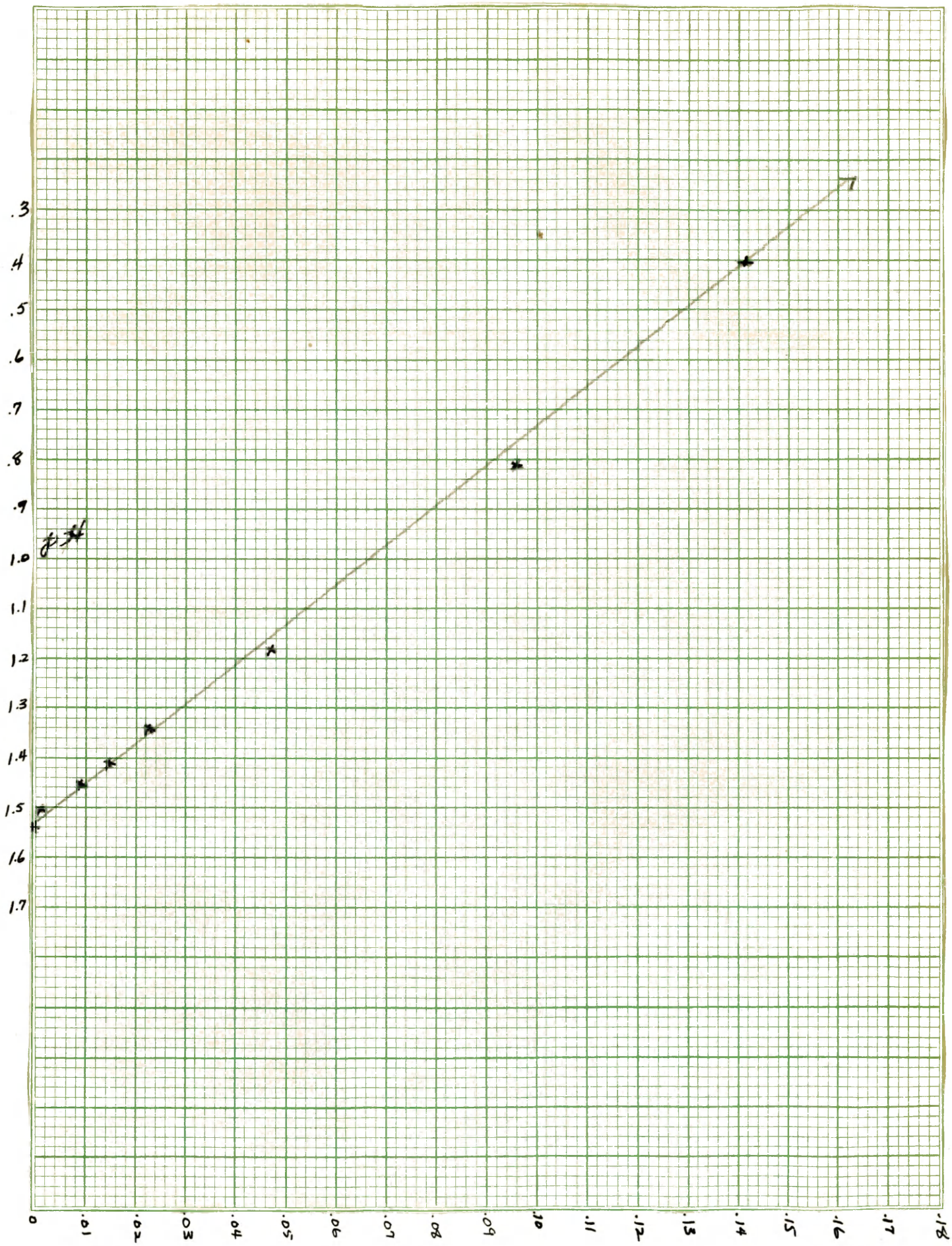


Graph 6. Mols NaCl added to 35 cc. 0.1 N H_2SO_4.

TABLE VII

LiCl with 35 cc. 0.1 N. H_2SO_4 t is 25° C.
(Hydrogen electrode)

LiCl (Grams)	Mols LiCl	Volts I	Volts II	pH
0.0	0.0	0.3088	0.3088	1.[illegible]
0.2	0.0047	0.3060	0.3060	1.[illegible]
0.4	0.0094	0.3037	0.3030	1.447
0.6	0.0141	0.3005	0.3005	1.405
1.0	0.0236	0.2970	0.2967	1.342
2.0	0.0472	0.2857	0.2850	1.179
4.0	0.0944	0.2669	0.2665	0.819
6.0	0.1416	0.2606	0.2606	0.682

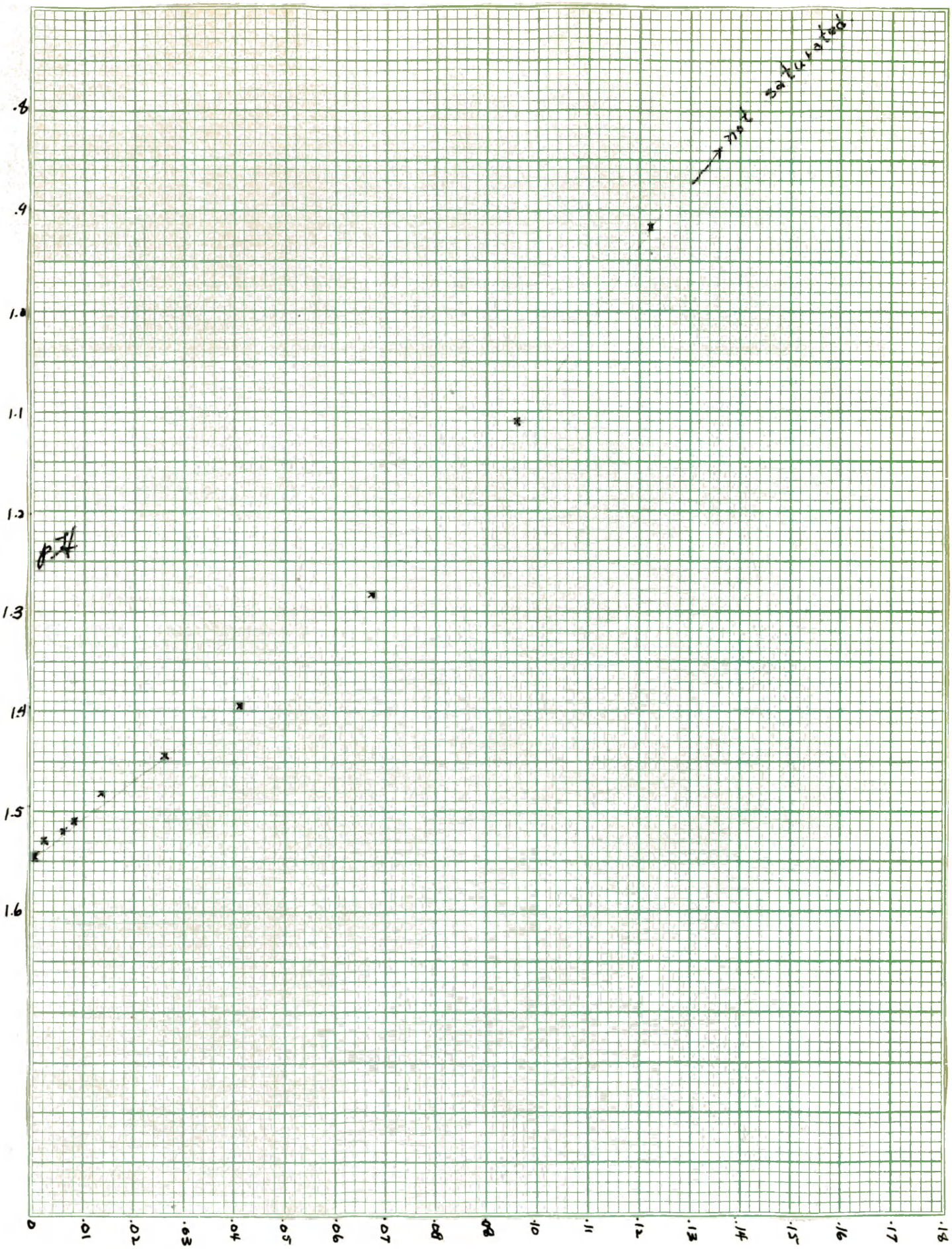


Graph 7. Mols LiCl added to 35cc. 0.1 N H_2SO_4.

TABLE VIII

KCl with 35 cc. 0.1 N. H_2SO_4 t is 25° C.
(Hydrogen electrode)

KCl (Grams)	Mols KCl	Volts I	Volts II	pH
0.0	0.0	0.3068	0.3068	0.0
0.2	0.0027	0.3060	0.3062	0.0027
0.4	0.0054	0.3075	0.3075	0.0054
0.6	0.0081	0.3075	0.3075	0.0081
1.0	0.0135	0.3057	0.3058	0.0135
2.0	0.0269	0.3052	0.3050	0.269
3.0	0.0404	0.2997		0.404
5.0	0.0673	0.2952	0.2950	0.0673
7.0	0.0942	0.2910		0.0942
9.0	0.1211	0.2705		0.1211

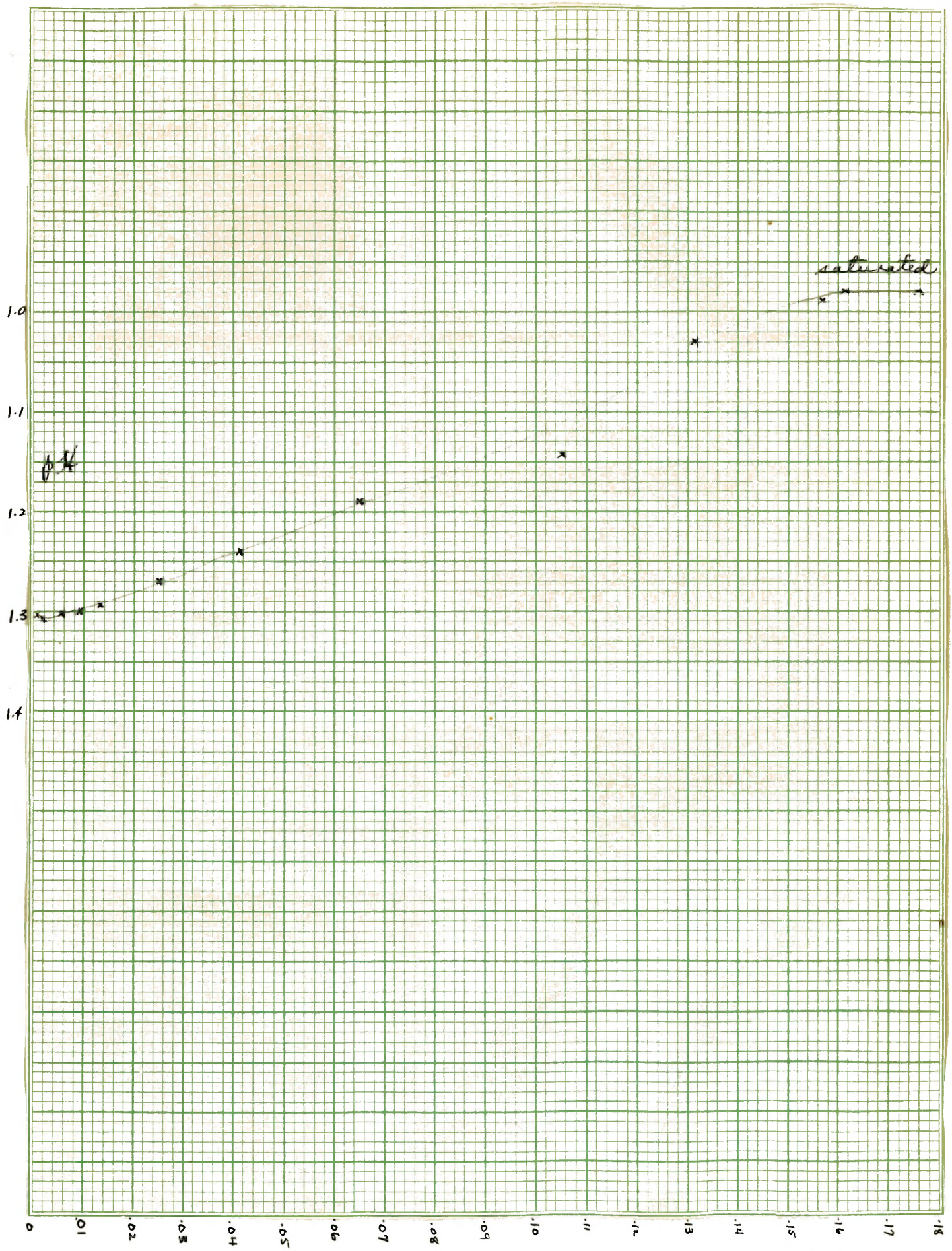


Graph 8. Mols KCl added to 35 cc. 0.1 N H_2SO_4.

TABLE IX

KCl with 35 cc. 0.1 N. H_2SO_4 t = 27° C.
(Quinhydrone electrode)

KCl (Grams)	Mols KCl	Volts I	Volts II	pH
0.0	0.0	0.3816	0.3881	1.308
0.2	0.0027	0.3810	0.3881	1.313
0.4	0.0054	0.3815	0.3881	1.308
0.6	0.0081	0.3815	0.3882	1.304
1.0	0.0135	0.3820	0.3884	1.296
2.0	0.0269	0.3835	0.3841	1.271
3.0	0.0404	0.3851	0.3855	1.244
5.0	0.0675	0.3881	0.3885	1.193
7.0	0.0942	0.3915	0.3921	1.136
9.0	0.1211	0.3947	0.3952	1.082
11.0	0.1480	0.3974	0.3985	1.037
13.0	0.1615	0.3982	0.3989	1.024
15.0	0.1750	0.3982		1.024

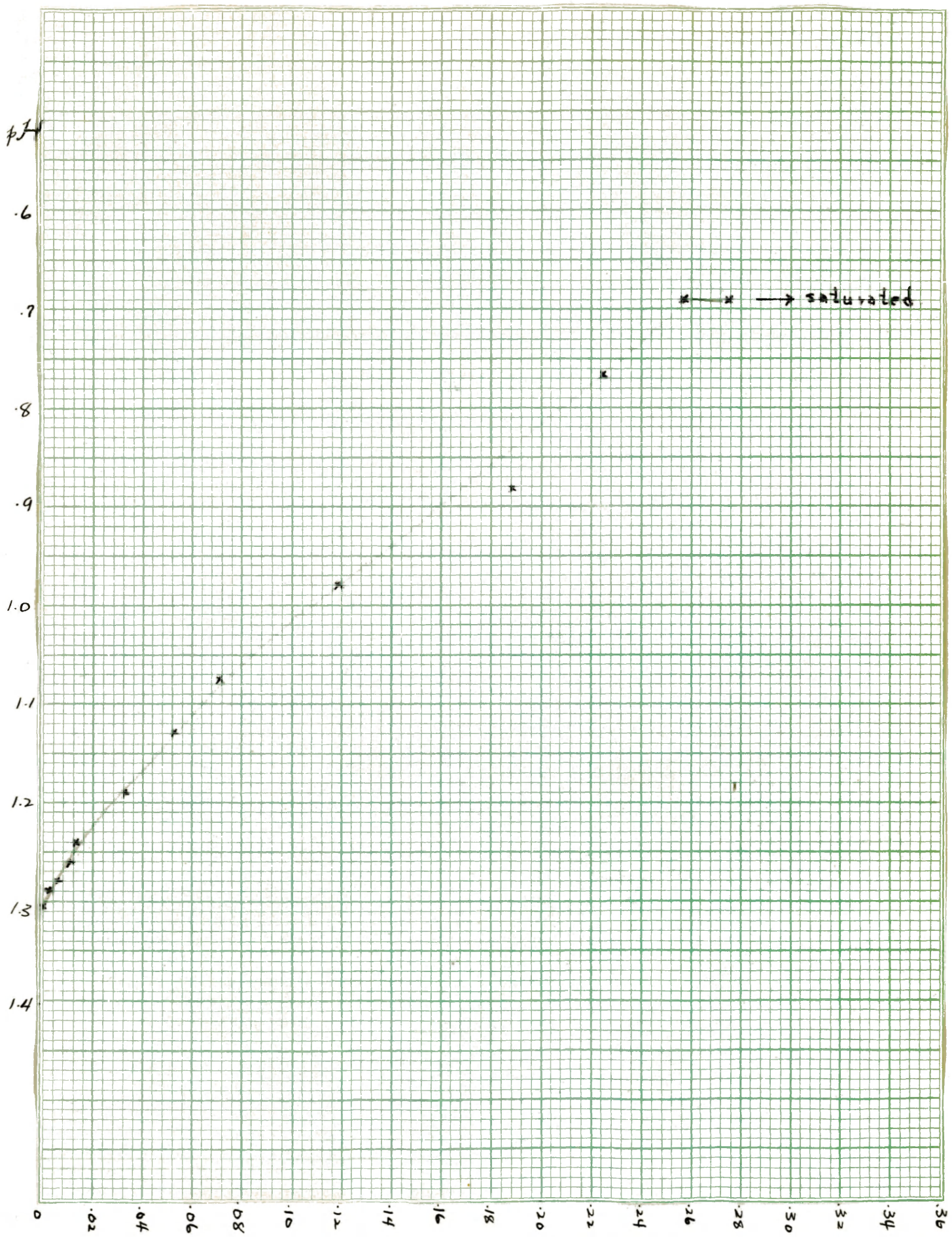


Graph 9. Mols KCl added to 35 cc. 0.1 N H_2SO_4. (Quinhydrone electrode).

TABLE X

NaCl with 35 cc. 0.1 N. H_2SO_4 (Quinhydrone electrode) t = 27° C.

NaCl (Grams)	Mols NaCl	Volts I	Volts II	pH
0.0	0.0	0.3816	0.3816	1.303
0.2	0.00342	0.3824	0.3824	1.289
0.4	0.00684	0.3832	0.3831	1.277
0.6	0.01026	0.3840	0.3838	1.256
1.0	0.0171	0.3852	0.3852	1.242
2.0	0.0342	0.3894	0.3894	1.190
3.0	0.0513	0.3917	0.3917	1.153
4.0	0.0684	0.4030	0.3950	1.077
6.0	0.1197	0.4009	0.4010	0.977
8.0	0.1881	0.4071	0.4078	0.873
10.0	0.2225	0.4135	0.4136	0.797
12.0	0.2565	0.4181	0.4181	0.699
13.0	0.2736	0.4181	0.4181	0.699



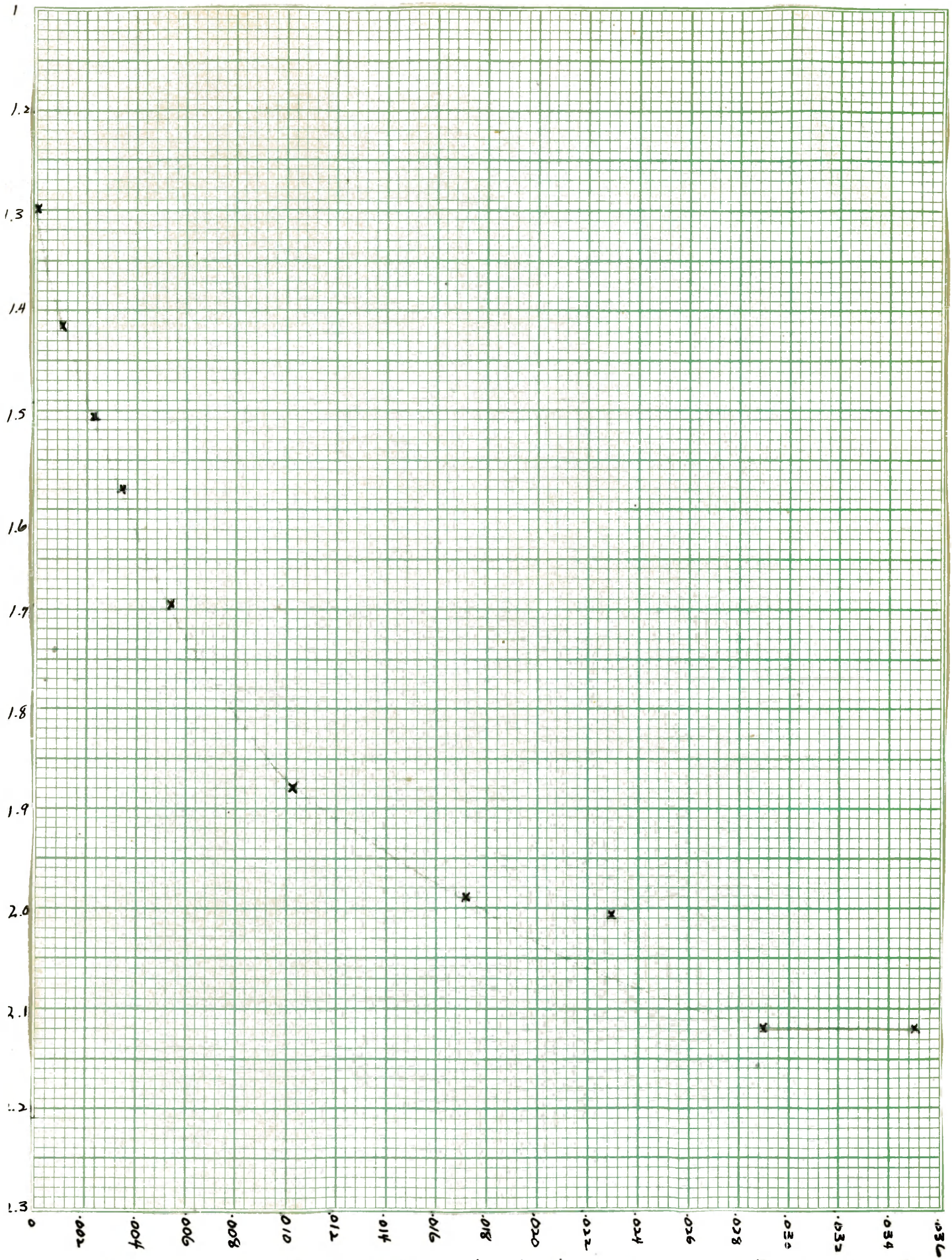
Graph 10. Mols NaCl added to 35 cc. 0.1 N H_2SO_4. (Quinhydrone)

TABLE XI

K_2SO_4 with 35 cc. 0.1 N. H_2SO_4 (Quinhydrone electrode)

t for Volts I = 27° C.
t for Volts II = 25° C.

K_2SO_4 (Grams)	Mols K_2SO_4	Volts I	Volts II	pH
0.0	0.0	0.3816	0.3815	1.305
0.2	0.00115	0.3749	0.3747	1.415
0.4	0.0023	0.3691	0.3691	1.515
0.6	0.00345	0.3646	0.3646	1.589
1.0	0.00575	0.3577	0.3578	1.704
2.0	0.0115	0.3475		1.879
3.0	0.0172	0.3407	0.3406	1.990
4.0	0.023	0.3353		2.080
5.0	0.0287	0.3327	0.3326	2.124
6.0	0.0345	0.3327	0.3326	2.124

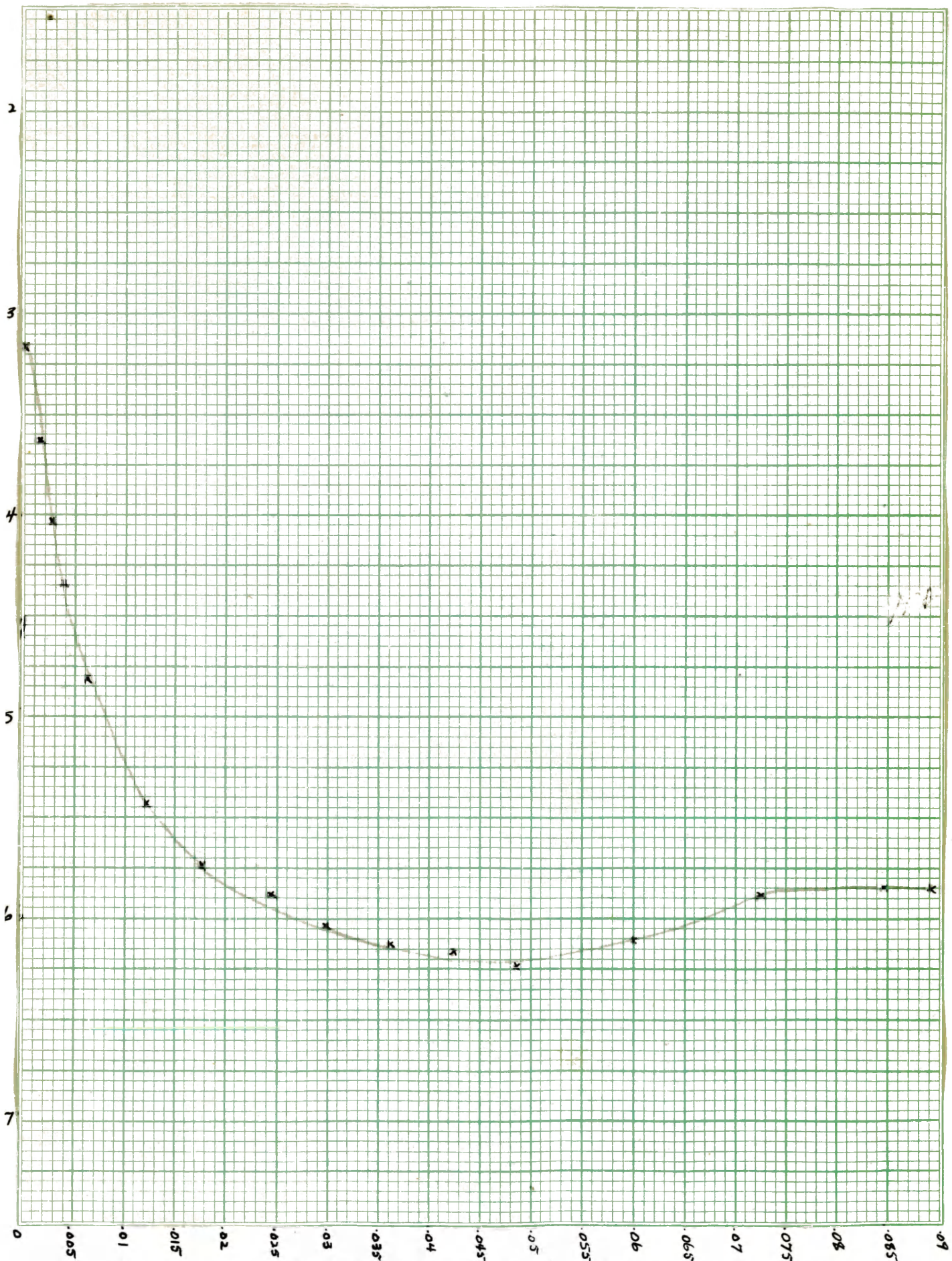


Graph 11. Mols K_2SO_4 added to 35cc. 0.1 N H_2SO_4 (Quinhydrone).

TABLE XII

$CuSO_4$ (Crystalline) with 35 cc. 0.1 N. H_2SO_4
(Quinhydrone electrode)

$CuSO_4$ (Grams)	Mols $CuSO_4$	Volts I	Volts II	pH
0.0	0.0	0.3810	0.3810	1.304
0.2	0.0012	0.3776	0.3776	1.361
0.4	0.0024	0.3754	0.3754	1.400
0.6	0.0036	0.3731	0.3731	1.436
1.0	0.0060	0.3702	0.3701	1.486
2.0	0.0119	0.3660	0.3660	1.556
3.0	0.0179	0.3638		1.576
4.0	0.0239	0.3632	0.3632	1.642
5.0	0.0299	0.3640		1.606
6.0	0.0359	0.3615		1.630
7.0	0.0419	0.3636		1.617
8.0	0.0479	0.3618		1.626
10.0	0.0598	0.3624	0.3625	1.615
12.0	0.0717	0.3634	0.3634	1.595
14.0	0.0836	0.3632	0.3632	1.569
15.0	0.0897	0.3632	0.3632	1.569



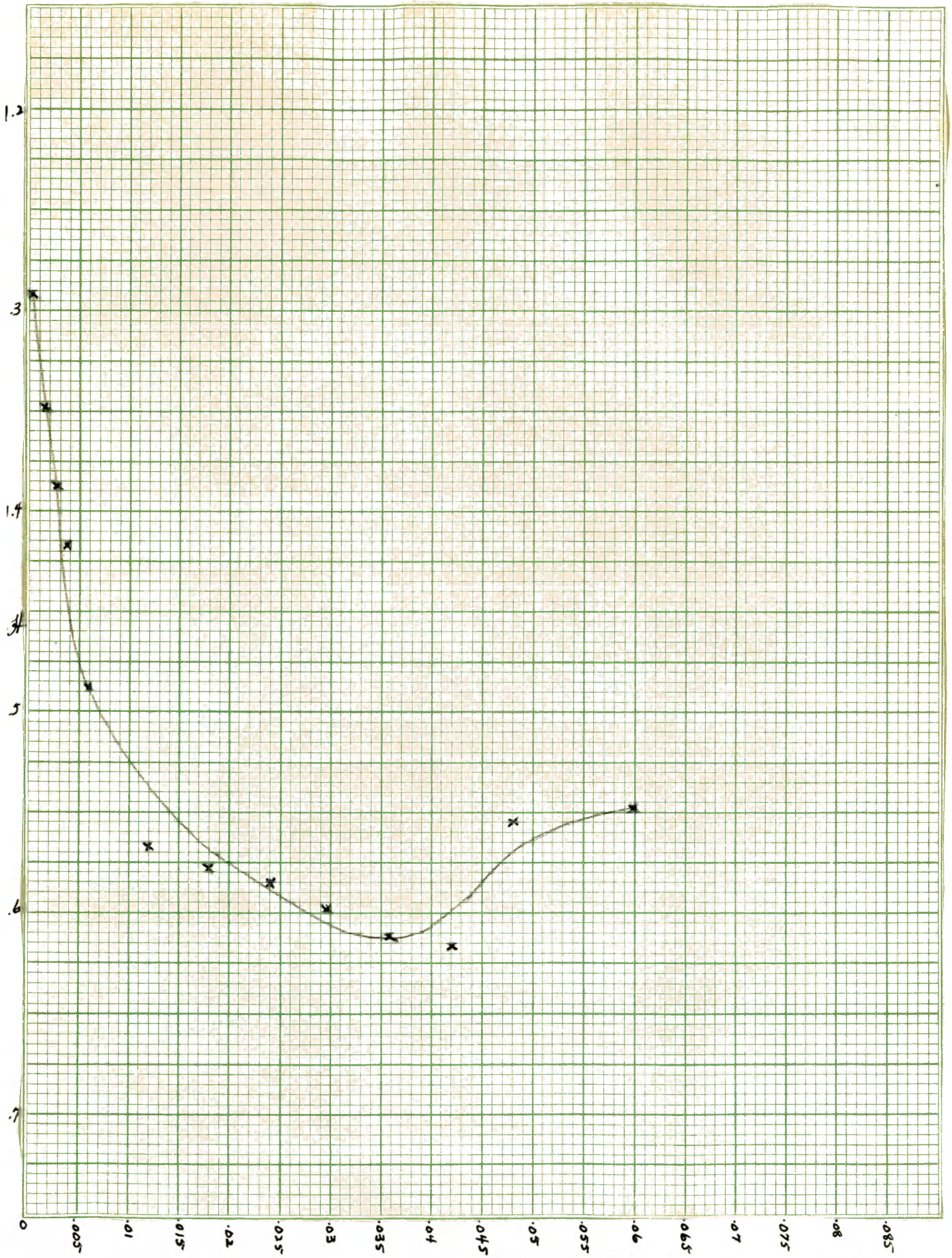
Graph 12. Mols $CuSO_4$ (crystalline) added to 35 cc. 0.1 N H_2SO_4. (Quinhydrone)

TABLE XIII

$CuSO_4$ (anhydrous) with 35 cc. 0.1 N. H_2SO_4
(Quinhydrone electrode)

t for Volts I = 26° C.
t for Volts II = 30° C.

$CuSO_4$ (Grams)	Mols $CuSO_4$	Volts I	Volts II	pH
0.0	0.0	0.3815	0.3815	1.289
0.2	0.0012	0.3780		1.348
0.4	0.0024	0.3755	0.3757	1.388
0.6	0.0036	0.3732		1.427
1.0	0.0060	0.3696	0.3695	1.487
2.0	0.0119	0.3648		1.567
3.0	0.0179	0.3645	0.3640	1.577
4.0	0.0239	0.3637		1.586
5.0	0.0299	0.3631		1.596
6.0	0.0359	0.3620		1.614
7.0	0.0419	0.3618	0.3620	1.617
8.0	0.0479	0.3655		1.556
10.0	0.0598	0.3660	0.3660	1.547

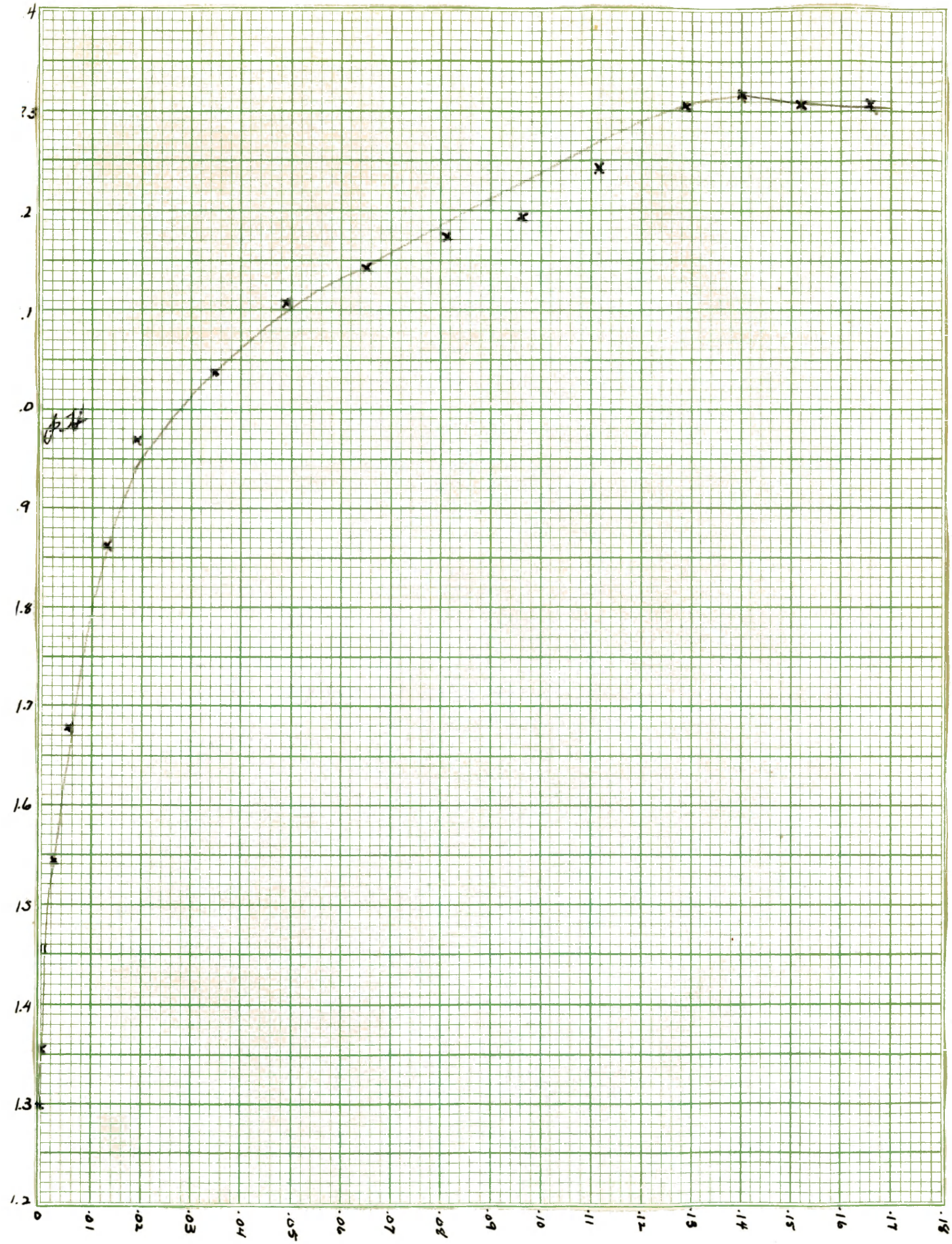


Graph 13. Mols $CuSO_4$ (anhydrous) added to 35 cc H_2SO_4 (Quinhydrone).

TABLE XIV

Na_2SO_4, 10 H_2O with 35 cc. 0.1 N. $MgSO_4$
(Quinhydrone electrode) t = 31° C.

(Grams) Na_2SO_4 10 H_2O	Mols Na_2SO_4 10 H_2O added	Volts I	Volts II	pH
0.0	0.0	0.3814	0.3814	1.287
0.2	0.00062	0.3777	0.3779	1.347
0.6	0.00186	0.3718	0.3718	1.446
1.0	0.0031	0.3664	0.3664	1.535
2.0	0.0062	0.3584	0.3582	1.670
4.0	0.0124	0.3509(t?)	0.3472	1.854
6.0	0.0186	0.3467(t?)	0.3405	1.965
11.0	0.0341	0.3362	0.3365	2.038
16.0	0.0496	0.3323	0.3322	2.102
21.0	0.0651	0.3295	0.3295	2.148
26.0	0.0806	0.3276	0.3276	2.179
31.0	0.0961	0.3267	0.3268	2.195
36.0	0.1116	0.3245	0.3245	2.249
41.0	0.1271	0.3194	0.3195	2.314
45.0	0.1395	0.3196	0.3197	2.316
49.0	0.1519	0.3200	0.3200	2.305
53.0	0.1643	0.3200	0.3200	2.305

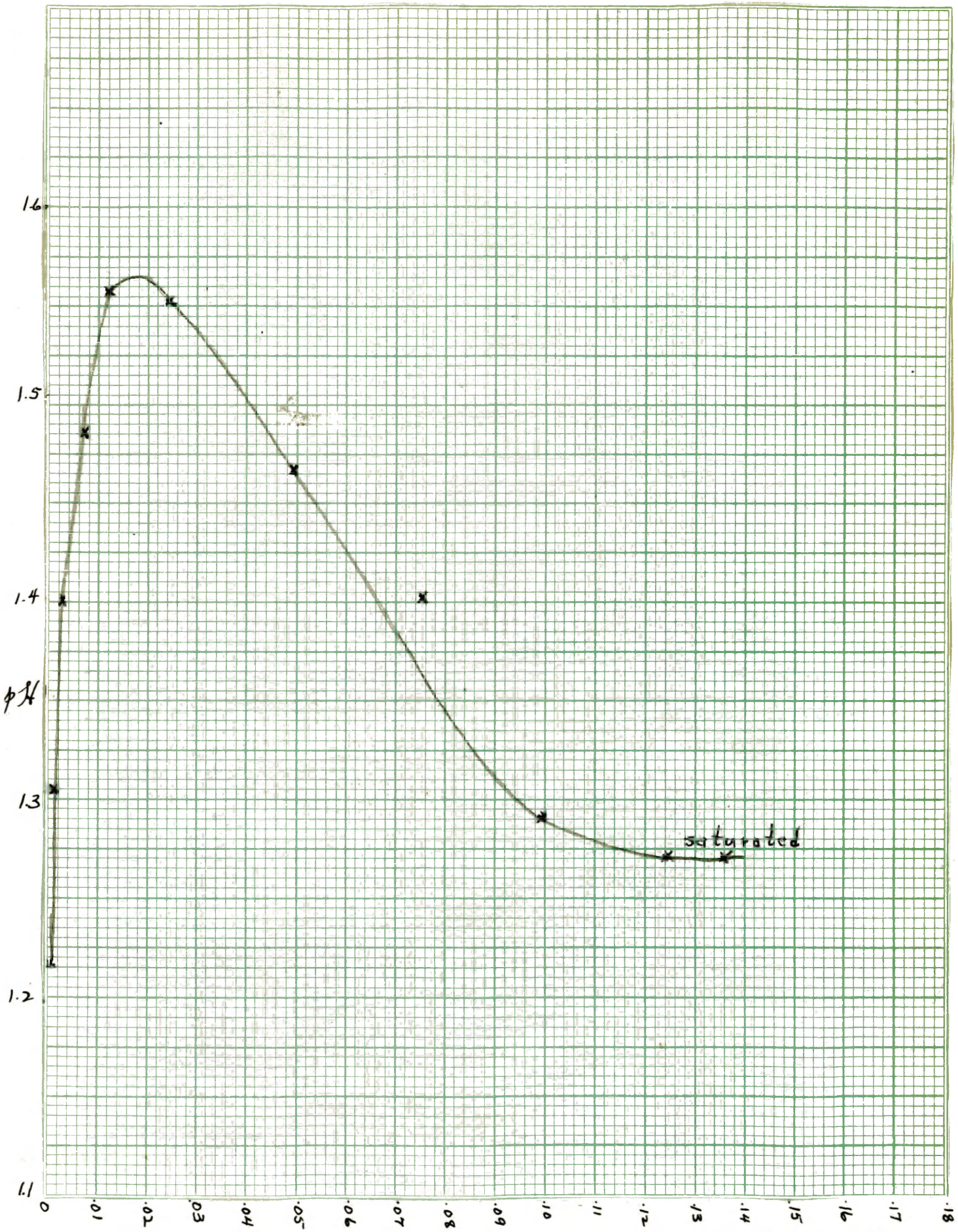


Graph 14. Mols $Na_2SO_4 \cdot 10H_2O$ added to 35cc. H_2SO_4.
(Quinhydrone)

TABLE XV

$ZnSO_4$ with 35 cc. 0.1 N. H_2SO_4 t = 38° C.
(Quinhydrone electrode and
Calomel electrode No. 2)

$ZnSO_4$ (Grams)	Mols $ZnSO_4$ added	Volts	pH
0.0	0.0	0.3801	1.217
0.2	0.00124	0.3748	1.305
0.6	0.00372	0.3691	1.400
1.0	0.00619	0.3640	1.484
2.0	0.01238	0.3597	1.556
4.0	0.02476	0.3600	1.551
8.0	0.04952	0.3651	1.466
12.0	0.07428	0.3685	1.409
16.0	0.09904	0.3720	1.285
20.0	0.1238	0.3769	1.270
24.0	0.13618	0.3769	1.270

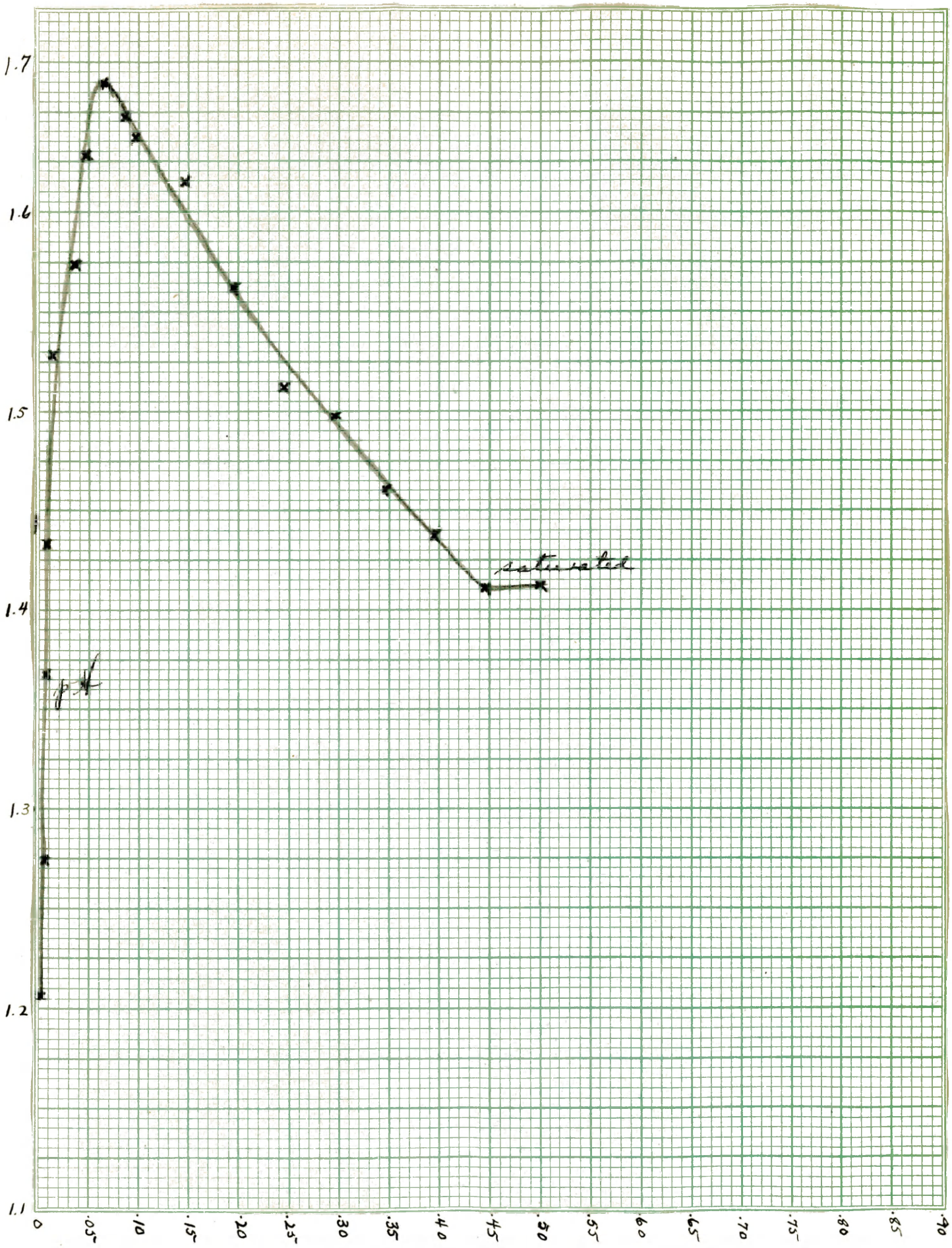


Graph 15. Mols $ZnSO_4$ added to 0.1 N H_2SO_4 (35 cc.)
(Quinhydrone)

TABLE XVI

$MgSO_4$ with 35 cc. 0.1 N. H_2SO_4 t = 33° C.
(Quinhydrone electrode and
Calomel electrode No. 2)

$MgSO_4$ (Grams)	Mols $MgSO_4$ added	Volts I	Volts II	pH
0.0	0.0	0.3804	0.3801	1.305
0.2	0.00166	0.3765	0.3761	1.372
0.5	0.00498	0.3707	0.3704	1.364
1.0	0.0083	0.3667	0.3664	1.450
2.0	0.0166	0.3605	0.3605	1.550
4.0	0.0332	0.3561		1.600
6.0	0.0498	0.3545	0.3545	1.629
8.0	0.0664	0.3527		1.659
10.0	0.0830	0.3534	0.3534	1.647
12.0	0.0996	0.3541	0.3539	1.638
17.0	0.1454	0.3559	0.3554	1.610
22.0	0.1972	0.3592	0.3585	1.560
27.0	0.2490	0.3614	0.3610	1.530
32.0	0.2948	0.3625	0.3625	1.498
37.0	0.3456	(Not satur-	0.3647	1.461
42.0	0.3924	ated)	0.3660	1.439
47.0	0.4412		0.3674 (Saturated)	1.413



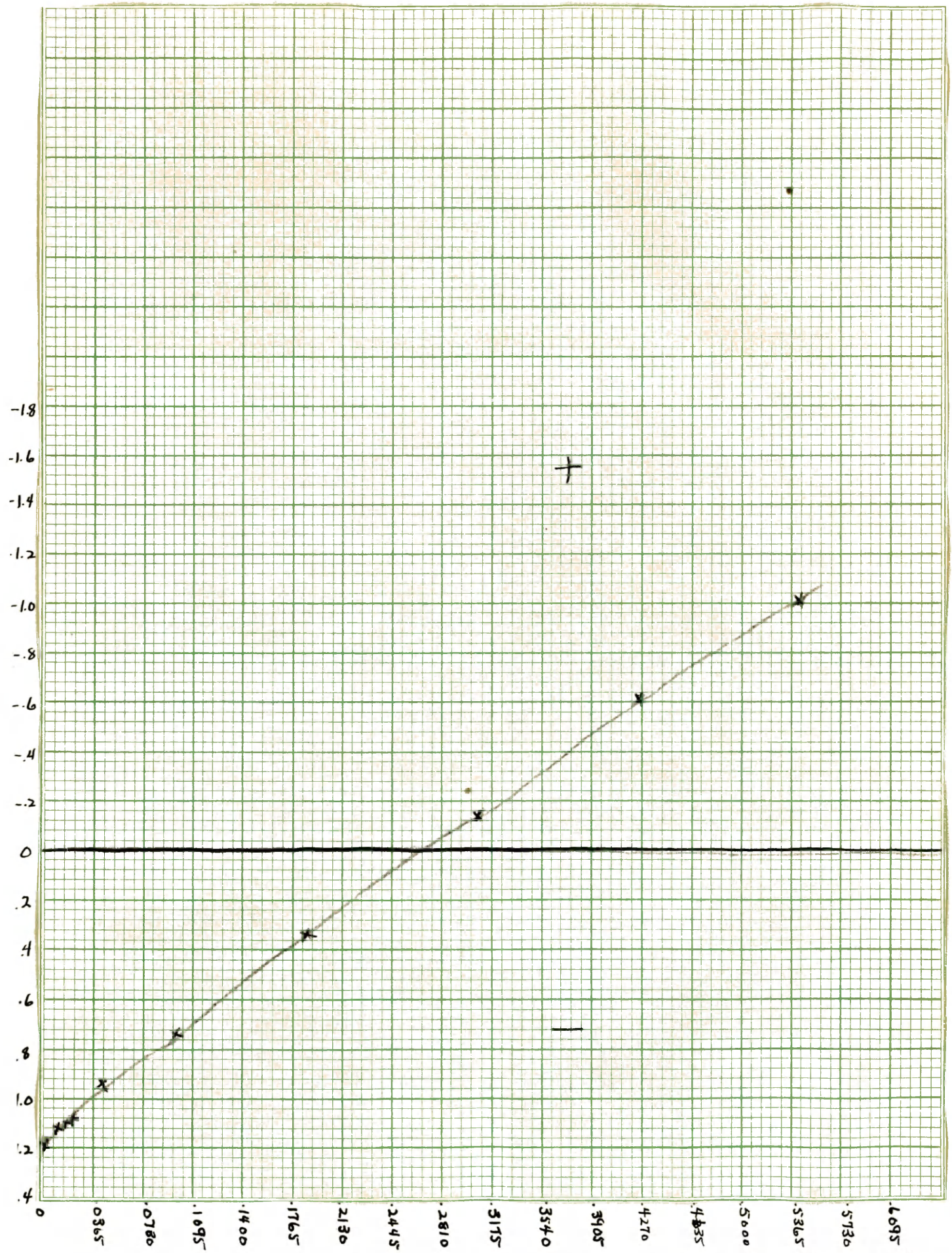
Graph 16. Mols $MgSO_4$ added to H_2SO_4. (Quinhydrone).

TABLE XVII

LiCl with 35 cc. 0.1 N. H_2SO_4
(Quinhydrone electrode and
Calomel electrode No. 2)

t for Volts I = 33°.
t for Volts II = 31°.

LiCl (Grams)	Mols LiCl added	Volts I	Volts II	pH
0.0	0.0	0.3801	0.3801	1.208
0.2	0.0047	0.3808	0.3819	1.190
0.4	0.0094	0.3824	0.3834	1.166
0.6	0.0141	0.3840	0.3843	1.145
1.0	0.0236	0.3871	0.3871	1.100
2.0	0.0472	0.3949	0.3949	0.988
3.0	0.0708	0.4022		0.845
4.0	0.0944	0.4081	0.4064	0.761
8.0	0.1888		0.4330	0.356
13.0	0.3068		0.4636	-0.187
18.0	0.4248		0.4909	-0.620
23.0	0.5428		0.5170	-0.025

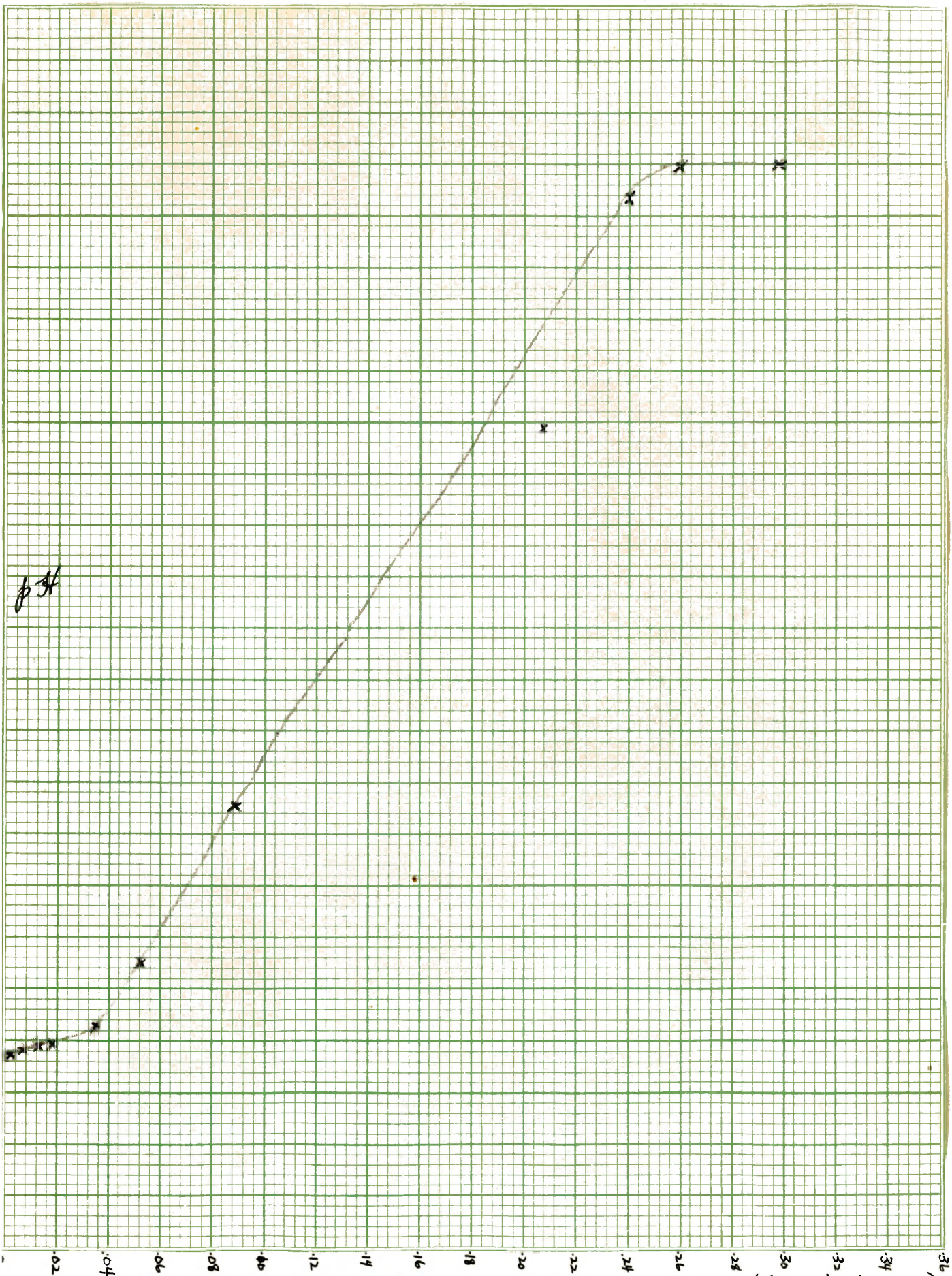


Graph 17. Mols LiCl added to 35 cc. 0.1 N H_2SO_4. (Quinhydrone)

TABLE XVIII

NaCl with 35 cc. 0.1 N. HCl (Quinhydrone electrode and Calomel electrode No. 2) t = 32° C.

NaCl (Grams)	Mols NaCl added	Volts I	Volts II	pH
0.0	0.0	0.3891	0.3891	1.069
0.2	0.00342	0.3888	0.3888	1.069
0.4	0.00684	0.3895	0.3895	1.065
0.6	0.01026	0.3905	0.3905	1.048
1.0	0.0171	0.3910	0.3908	1.038
2.0	0.0342	0.3927	0.3928	1.009
3.0	0.0513	0.3954	0.3956	0.964
5.0	0.0855	0.4004		0.881
8.0	0.1881	0.4098	0.4097	0.723
11.0	0.2594	0.4170		0.592
12.0	0.2565	0.4187		0.577
13.0	0.2736	0.4187	0.4187	0.577

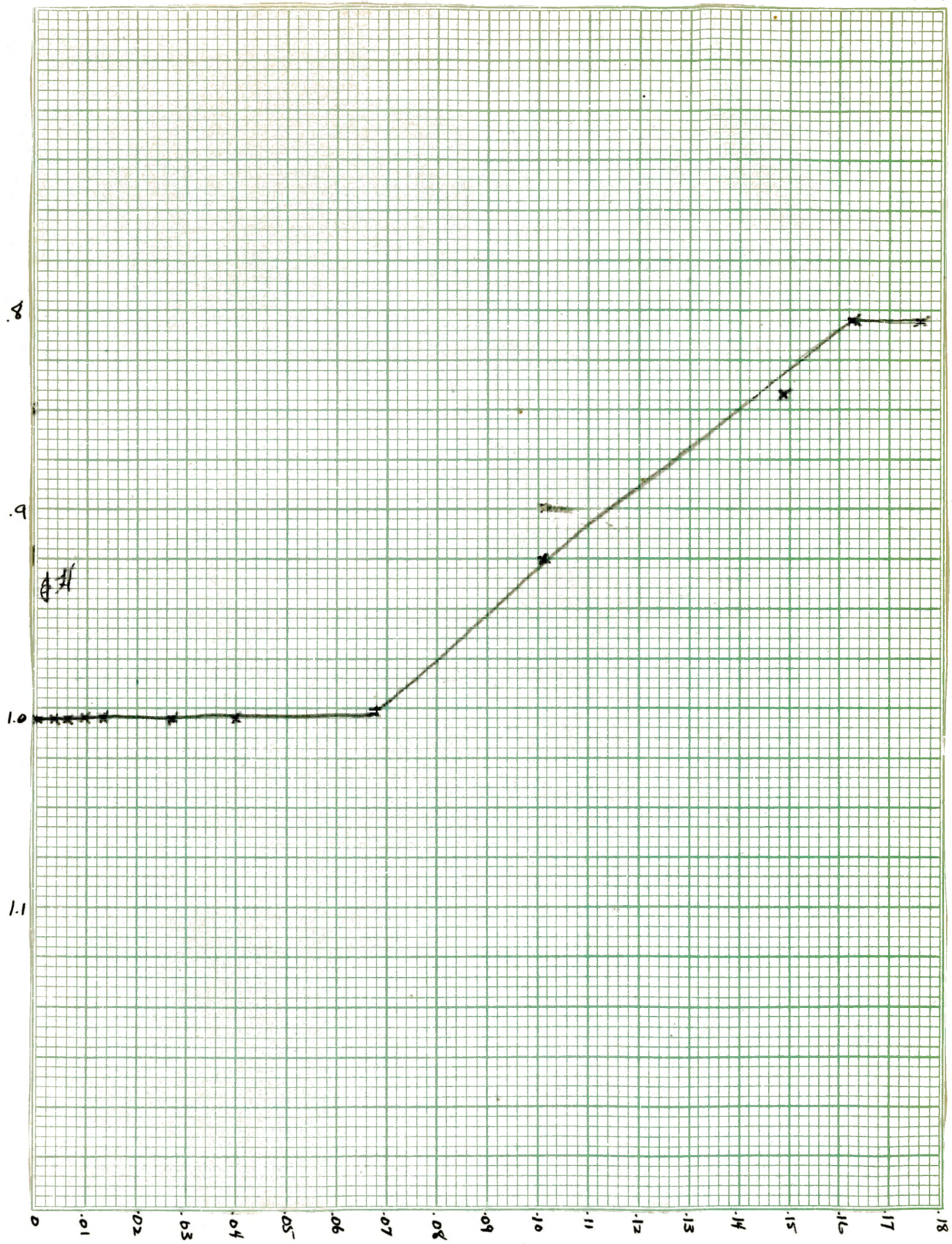


Graph 18. Mols NaCl added to 35cc 0.1 N HCl (Quinhydrone).

TABLE XIX

KCl with 35 cc. 0.1 N. HCl (Quinhydrone electrode and Calomel electrode No. 2) t = 32° C.

KCl (Grams)	Mols KCl added	Volts I	Volts II	pH
0.0	0.0	0.3891	0.3891	1.069
0.2	0.0027	0.3885	0.3885	1.078
0.4	0.0054	0.3883	0.3883	1.081
0.6	0.0081	0.3882	0.3882	1.083
1.0	0.0135	0.3882	0.3882	1.083
2.0	0.0269	0.3880		1.080
3.0	0.0404	0.3901	0.3901	1.051
5.0	0.0673	0.3939		1.006
8.0	0.1077	0.3978	0.3979	0.952
11.0	0.1481	0.4027		0.842
12.0	0.1616	0.4047		0.869
13.0	0.1751	0.4047	0.4047	0.869

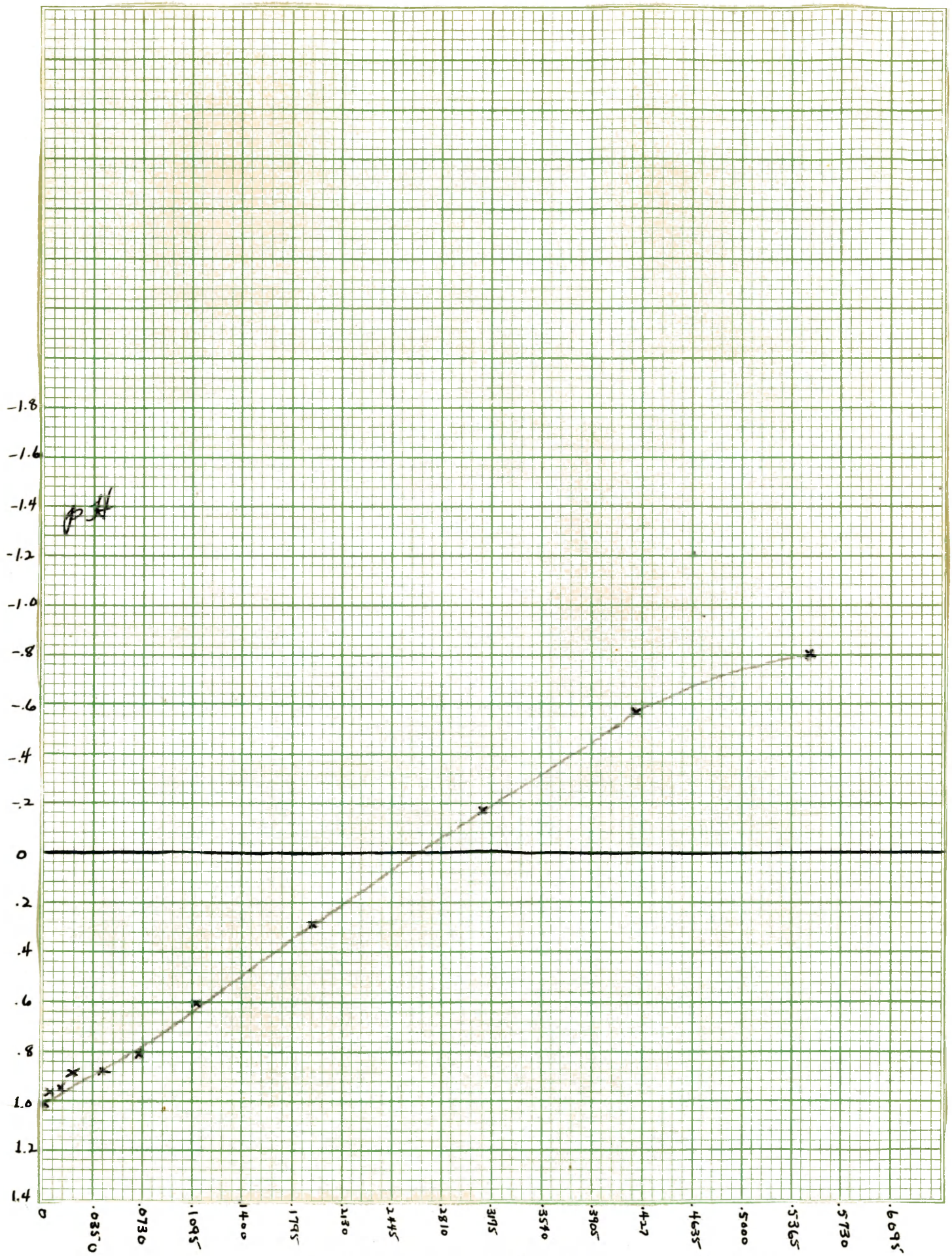


Graph 19. Mols KCl added to 35 cc. 0.1 N HCl.
(Quinhydrone).

TABLE XX

LiCl with 35 cc. 0.1 N. HCl (Quinhydrone electrode and Calomel electrode No. 2) t = 31° C.

LiCl (Grams)	Mols LiCl added	Volts I	Volts II	pH
0.0	0.0	0.3891	0.3891	1.069
0.2	0.0047	0.4906	0.3906	1.044
0.4	0.0094	0.3913		1.051
0.6	0.0141	0.3924	0.3928	1.010
1.0	0.0236	0.3942		0.980
2.0	0.0472	0.3988		0.907
3.0	0.0708	0.4045	0.4040	0.818
5.0	0.1180	0.4153	0.4155	0.628
8.0	0.1888	0.4349		0.308
13.0	0.3068	0.4647	0.4648	-0.196
18.0	0.4248	0.4898		-0.598
23.0	0.5428	0.5005	0.5006	-0.780



Graph 20. Mols LiCl added to 35 cc. 0.1 N HCl. (Quinhydrone)

KCl with HCl.

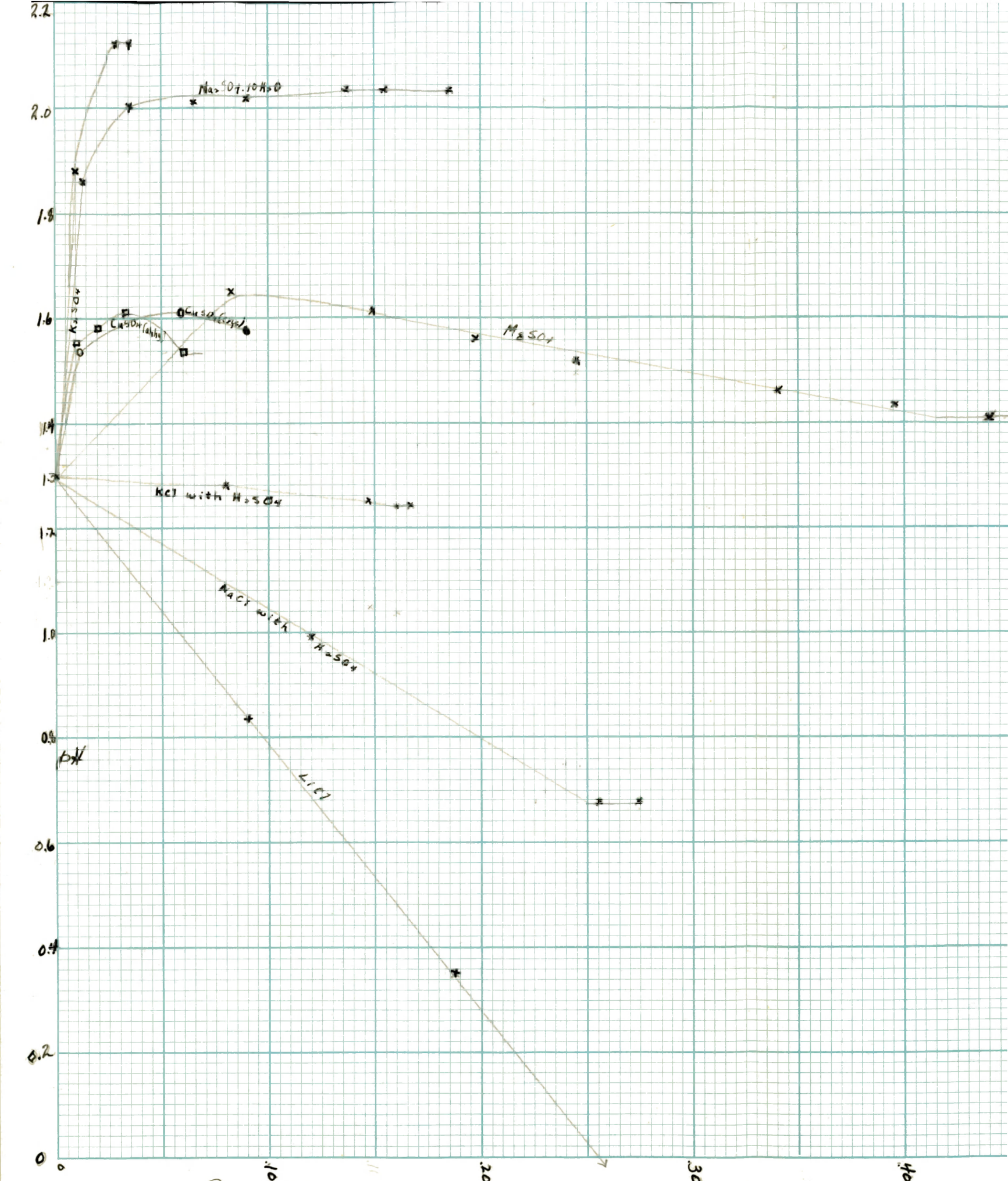
NaCl with HCl.

LiCl with HCl.

pH

Mols added

Graph 21.



Graph 22. Mols added to 35 cc. 0.1 N H_2SO_4

SUMMARY

It was found that the addition of chlorides, whether to tenth normal sulphuric acid or to tenth normal hydrochloric acid, increased the acidity in all cases. The addition of sulphates decreased the acidity of tenth normal sulphuric acid in all cases.

The sulphates of the monovalent metals had the greatest effect in decreasing the acidity, while the sulphates of the divalent metals showed interesting intermediate effects. The addition of the divalent salts showed a decrease in acidity up to a certain point, which was followed by an increase in acidity up to the saturation point. The sulphuric acid, however, never became more acid (due to the addition of the divalent sulphates) than it was before the addition of any of the solute.

CONCLUSIONS

From the results of this experiment the following conclusions were arrived at:

I. The increase in acidity of tenth normal hydrochloric acid due to the addition of potassium chloride, sodium chloride, and lithium chloride was proportional to:

(a) Atomic weights. The acidity increased as the atomic weight order decreased.

(b) Solubility of the salts. The acidity increased with an increase in the solubility.

(c) Transference numbers. The acidity increased with a decrease in the transference number of the positive ion.

(d) Hydrate formation. The acidity increased with an increase in the ease of hydration.

(Nothing can be said in regard to the effect of valency on acidity because the three salts used in this case were of monovalent metals).

II. The decrease in the acidity of tenth normal sulphuric acid, due to the addition of various sulphates, was proportional to:

(a) Atomic weights. The acidity decreased with a decrease in atomic weights.

(b) Valence. The sulphates of the monovalent metals decreased the acidity more markedly than the sulphates of the divalent metals.

III. The quinhydrone method proved superior to that of the hydrogen electrode in this experiment, as it was found that:

(a) Results could be reproduced more easily.

(b) A greater number of salts could be used.

(c) Measurements could be made more quickly.

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